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FINAL REPORT

DETERMINATION OF TEST METHODS FOR INTERIOR ARCHITECTURAL COATINGS

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SECTION 1.0
INTRODUCTION

Numerous building materials and consumer products are used in indoor environments. In recent years there has been increased awareness that exposure to pollutants indoors may occur due to emissions of volatile organic compounds (VOCs) from indoor materials and consumer products. Emissions of volatile organic compounds decrease over time, but many products are used on a repeated basis indoors. Some materials such as architectural coatings, for example, may be used periodically during remodeling and renovation of interior spaces.

The Office of Air and Radiation (OAIR) and the Office of Pollution Prevention and Toxics (OPPT) of the U.S. Environmental Protection Agency (EPA) have jointly undertaken a project to analyze the emissions of VOCs from various types of products used indoors. The ultimate goals of the project are to determine which types of products result in the greatest overall exposures to pollutants indoors and which specific chemical emissions from the products may present a risk to the populations exposed. Critical to the performance of this project is the use of appropriate techniques to evaluate emissions of total and specific VOCs from these sources.

A preliminary study was performed by Research Triangle Institute (RTI) for the EPA in 1992 (1). This preliminary study used an alkyd and a latex interior architectural coating (IAC) to evaluate seven methods that might be used to determine product content or emissions of organic compounds from IACs. This work assignment is a followup to the preliminary work and is intended to provide a more detailed analysis of three of those methods; ASTM standard methods, bulk product analysis, and small chamber testing.

The purpose of this work assignment was the determination of definitive, valid methods to test for VOCs, semivolatile organic compounds (SVOCs), total volatile organic compounds (TVOCs), aldehydes, and metals in interior architectural coatings. The specific objectives of the work assignment were:

- To perform an evaluation of selected test methods that can be used to characterize the composition, and for small chamber testing, the rate of VOC/SVOC and aldehyde emissions from architectural coatings used indoors;

- To perform an evaluation of test methods for the determination of the content of metals in these coatings;
- To compare the data obtained by the test methods for VOCs/SVOCs, aldehydes, or metals;
- To obtain definitive, valid test methods for the determination of VOC/SVOC and aldehyde emissions from and metal content in IACs; and
- Estimate the cost of performing subsequent analyses using each method.

This report describes the study methods. Analytical results, quality assurance/quality control results, method evaluation results, and methods comparisons are also given. Costs for routine testing of IACs by the finalized methods have been estimated and are provided.

SECTION 2.0
SUMMARY

This study was conducted to provide an evaluation of selected methods to characterize the composition and/or rate of emissions for VOCs, SVOCs, and aldehydes from architectural coating used indoors. It was also designed to evaluate methods for the determination of metal content in these coatings. Test methods were evaluated using ten latex paints and ten alkyd paints. Paints were selected from commercially available brands to provide a range of gloss types and colors. Tests were replicated to provide information on method precision. Five different methods were evaluated. Table 2-1 briefly summarizes the methods and their potential applicability to testing of alkyd and latex paints. Prior to testing with paint samples, modifications to methods used previously (1) were evaluated and incorporated into the methods to improve performance.

2.1 ASTM METHODS

The ASTM methods for gravimetric determination of the volatile content of the paint and the determination of water by the Karl Fischer method were easily performed. These data were then used to estimate total volatile organic concentration in the paints. The volatile content of the alkyd paints ranged from 30 to 55% by weight. The water content for all of the six alkyd paints tested was less than 1%. TVOC concentrations were therefore nearly equivalent to the volatile content, ranging from 29 to 54%. For the six latex paints tested, the water content ranged from 45 to 55%, the volatiles ranged from 55 to 65%, and the TVOC ranged from 3.5 to 9.5%. The precision of the method was excellent, with relative standard deviations (RSDs) less than 0.6% for the gravimetric determinations. The precision of the Karl Fisher method for water determinations was also very good. For the latex paints RSDs were less than 2.5%. For the alkyd paints, RSD values were higher (1.4 to 17%) but this reflects the very low water content found in these samples. The costs for these determinations are relatively low (approximately $40 to $50 per sample).

TABLE 2-1. TEST METHODS EVALUATED IN THE STUDY FOR INTERIOR ARCHITECTURAL COATINGS

Method	Collection/Preparation Method	Analysis[a] Method	Information Collected	Approximate Cost per Analysis	Applicability
ASTM D2369 ASTM D4017	—	Gravimetric Karl Fischer	% Volatile content % Water	\$20 \$50	ASTM standard method
Direct analysis	Dilution in solvent	GC/MS	Compound identification and quantitation	\$100-250	Inexpensive - may be used to identify important components for emission
Small chamber	Collection on charcoal tubes, solvent desorption with CS_2	GC/MS	Emission rates over time for TVOC and individual VOCs from alkyd paint	\$2,000-3,500	Data can be used to estimate concentrations over time and decay in indoor environments
	Collection on Tenax TA, thermal desorption	GC/FID	Emission rates over time for TVOC and individual SVOCs from alkyd paints	\$2,000-3,500	Data can be used to estimate concentrations over time and decay in indoor environments
ICP	Acid digestion	ICP	Metals content of paint	\$50-75	Suitable for quantitating metals in paint samples
XRF	—	Direct XRF of paint	Metals content of paint	\$30-60	May identify metals in paint samples

[a]GC/MS - Gas chromatography/mass spectrometry.
ICP - Inductively coupled plasma emission spectroscopy.
XRF - X-ray fluorescence spectroscopy.

2.2 BULK ANALYSIS OF PAINT SAMPLES

Analysis of the liquid paint samples diluted in an appropriate solvent and analyzed by gas chromatography/mass spectrometry (GC/MS) provided information on the individual target analytes that could be expected to occur in the emissions from the paint and on TVOC concentration.

The alkyd paints contained hundreds of compounds that are predominately branched chained hydrocarbons. For the gloss and semigloss alkyd paints tested, there was a higher relative abundance of the more volatile species compared to the flat finish paints. The most abundant target VOCs for paints with the gloss and semigloss finish were m,p-xylene, n-nonane, n-decane, and n-undecane. For the flat alkyd paint the most abundant compounds were n-undecane, n-dodecane, m,p-xylene, and n-decane. Concentrations for VOCs in alkyd paints ranged from 0.5 to 10 mg/g of paint. TVOC concentrations were in the range 300 to 500 mg/g of paint.

In contrast, the latex paints contained relatively few volatile organic chemicals. The SVOCs identified during analysis generally accounted for all of the components in the GC/MS chromatogram. For the various paint samples tested, the presence and relative abundance of individual VOCs varied between samples with no clear trend for gloss type. For four of the six latex paints, ethylene glycol was the most abundant compound (19 to 40 mg/g). 1,2-Propanediol (~38 mg/g) and 2-(2-methoxyethoxy)ethanol (23 mg/g) had the highest concentration in the other two paint samples. Other compounds with relatively high concentrations (>10mg/g) included 2-(2-butoxy-ethoxy)ethanol, and Texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate).

Duplicate samples were analyzed for selected paint samples as a way to assess uniformity of the sample aliquots as well as overall method precision. Results showed low %RSD values (generally less than 10%) for both paint types. These results suggest that both the replicate sample aliquots were uniform and the precision of the overall method was good.

2.3 SMALL CHAMBER METHOD

The small chamber test method provided quantitative data that could be used to estimate emission rates for VOCs, SVOCs and, aldehydes from paint samples. A set of 22 chamber tests were performed, 11 each for the alkyd and latex paints. Preliminary tests were performed as range finding tests to determine the appropriate air sample collection volumes, sample collection time points, and test durations for the two types of paints. Duplicate tests were performed to determine the recovery of target VOCs/SVOCs from the chamber. Sets of single chamber repeatability and interchamber variability tests were then performed to obtain emissions data and results on the performance of the chamber emissions method using alkyd and latex paints of different gloss types. Finally, chamber tests for an alkyd and a latex paints were performed to evaluate the effect of air velocity on emission rates. Results were compared with and without a fan operating in the chamber.

Data reported for each chamber test included chamber air concentration (mg/m^3) and chamber air concentration (mg/m^3) per gram of paint applied in the chamber at each sampling point . These data were then applied to various models to estimate emission parameters for each of the target VOCs, SVOCs, TVOC, and aldehydes. Emission parameters included the initial source strength (mg/h.g of paint) and emission decay constants (h^{-1}). The resulting parameters were then used to estimate the total mass of each target VOC/SVOC and TVOC emitted per gram of paint during testing.

For the chamber recovery tests, good recoveries were calculated for all of the test compounds under constant concentration conditions suggesting minimal losses of target VOCs and SVOCs during emissions testing. Results generated between test chambers were similar suggesting good reproducibilty for the overall chamber test method.

Results of the chamber tests for the alkyd paint samples showed highest chamber air concentrations for the n-alkanes (n-decane, n-nonane, and n-undecane). For the more volatile compounds, the highest chamber air concentrations were seen for the earliest sample collection points. In contrast, the highest chamber air concentrations for the less volatile compounds were seen at the later time points. For the flat and semigloss alkyd paints, chamber air concentrations for the least volatile compounds (i.e., 2-methyldecane, trans-decahydronaphthalene, n-undecane, pentylcyclohexane, and n-dodecane) were still relatively high at the end of the 24-hour test period. This was in contrast to the concentration measurements for these same compounds measured for the gloss paint. These chamber concentration results are consistent with visual observations where the flat and gloss paints were still tacky when removed from the chamber after testing. Variability between tests using the same paint was evaluated as the %RSD between paired chamber air concentrations for the two tests. For most cases, RSD values were less than 30% indicating acceptable reproducibility. Highest %RSD values were calculated for the latter time points were chamber air concentrations were low.

For the alkyd paints, a final set of chamber emissions tests were performed to evaluate the effect of air surface velocity on VOC emissions. Results for the test with the fan (surface air velocity ~10 cm/sec) showed higher air concentrations at the earlier time points with a more rapid decrease in air concentration when compared to results for the test without the fan (surface air velocity < 2 cm/sec). In the absence of a fan the less volatile components still showed relatively high chamber air concentration at the end of the 24-hour test period.

Results from applying the chamber air concentration data to emission models showed that a decaying source model represented most of the VOCs and TVOCs in the alkyd paint quite well. Relatively poor fits were seen for compounds with the lowest chamber air concentrations. Best fits were seen for the TVOC data. Chamber air concentrations for the more volatile VOCs appeared to peak at approximately 5 hours. For the less volatile VOCs, particularly n-dodecane and pentylcyclohexane, the chamber air concentrations appeared to peak well beyond five hours, but there were not sufficient data points beyond this time to define parameters for a slow buildup model. For these less volatile components, the present models do not define the chamber air concentration very well. When the chamber tests were performed with the fan, the models did a better job of describing the chamber air concentrations, especially for the less volatile species.

Results of the single chamber repeatability and interchamber variability tests for the latex paint samples showed several trends.

- Reproducibility between paired tests both within a single chamber and across chambers was generally good (%RSD values >30).
- Greatest variability between paired samples was generally found when air concentrations were low.
- For all paint types, measured air concentration for ethylene glycol were high (>60 mg/m^3).
- For the semigloss paint, air concentration for 1,2-propanediol were very high (>200 mg/m^3).

- Chamber air concentration for target SVOCs gradually increased over time with highest concentrations measured at either 24 or 48 hours. After that time, concentrations showed a gradual decrease.
- For the semigloss paint, all target SVOCs were at relatively low concentrations at the end of the 168-hour test period with only 2-(2-butoxyethoxy)ethanol at measurable levels. In contrast, relatively high concentrations of ethylene glycol were still present in the chamber air samples for the flat paint (Tables 8-26 and 8-27) and the gloss paint (Tables 8-28 and 8-29).

Tests performed to evaluate the effect of surface air velocity on SVOC emissions from latex paint samples showed the same trends as seen for the alkyd paints. Basically, the test performed with the fan showed higher air concentrations at the earlier time points with a more rapid decrease in air concentrations over time when compared to the paired test without the fan.

The chamber air concentrations for most of the SVOCs and TVOC emitted from the latex paint were best described using a slow buildup model. This model did not perform as well for these emissions as the decaying source model performed for the VOCs emitted from the alkyd paints. However it did appear to capture the general pattern of latex emissions. The poorer agreement between measured and modeled concentrations may be due to the fact that these relatively polar and less volatile SVOCs are more difficult to analyze and as a result may have more variability associated with the measured chamber air concentrations.

Finally, the emission models were used to estimate the mass of each VOC/SVOC and TVOC emitted per gram of paint during the small chamber tests. This information is given in Table 2-2 for the tests with the alkyd paints. The table also gives the mass of each VOC and TVOC per gram of paint measured during bulk product analysis of the same paint samples. The difference between the estimated mass emitted and the mass measured in the bulk paint samples is presented as the %RSD calculated for the two measures. For TVOC, the mass per gram of paint estimated from the ASTM methods is also given. Similar data are given for the latex paints in Table 2-3. Results generally show good agreement between the two measures suggesting that the chamber data and models can be used to describe the organic emissions from paint samples. Poorest agreement is seen for some of the less volatile VOCs in the alkyd paint where sufficient chamber data were not available to adequately

TABLE 2-2. COMPARISON OF DATA FOR CHAMBER EMISSIONS TESTS TO RESULTS FOR BULK PRODUCT ANALYSIS FOR ALKYD PAINTS

	GL[a]-Gloss (Hyacinth) Tests 5 and 6			GL - Flat (Chim Cham) Tests 11 and 12			GL - Semigloss (Sea Foam) Tests 13 and 14			SW[b] - Gloss (Bumbershoot) Test 21			SW[b] - Gloss (Bumbershoot) Test 22		
Compounds	Me[c] (mg/g)	C_b[d] (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD
m,p-Xylene	2.3	3.6	31	1.3	1.6	13	2.7	4.0	27	3.4	4.3	16	3.1	4.3	23
n-Nonane	6.9	9.8	25	0.90	0.68	20	4.6	5.3	10	13	11	9	11	11.2	2.6
o-Xylene	0.76	1.1	26	0.41	0.37	8	0.98	1.1	7	0.65	0.83	17	0.65	0.83	17
Propylcyclohexane	2.6	4.2	33	0.26	0.20	18	1.1	1.5	19	3.0	3.4	9	3.0	3.4	9
3- & 4-Ethyl toluene	1.9	1.8	3.8	0.26	ND[e]	–	1.5	1.3	10	0.39	ND	–	0.34	ND	–
1,3,5-Trimethylbenzene	0.82	0.79	2.8	0.10	ND	–	0.61	0.52	11	0.15	ND	–	0.18	ND	–
n-Decane	21	18	11	5.0	4.5	7	5.9	14	58	25	19	18	20	19	2.5
2-Ethyl toluene	0.51	0.62	13	0.090	ND	–	0.42	0.48	10	0.13	ND	–	0.12	ND	–
1,2,4-Trimethylbenzene	2.6	2.8	4.2	0.31	ND	–	2.0	1.8	7	0.46	0.53	10	0.44	0.53	14
1,2,3-Trimethylbenzene	0.9	0.84	7	0.12	ND	–	0.81	0.64	17.1	0.19	ND	–	0.13	ND	–
2-Methyldecane	1.9	2.0	3.7	2.2	3.2	2.7	3.3	2.6	16	3.9	3.2	13.1	4.3	3.2	21
trans-Decahydronaphthalene	2.4	2.1	8.5	3.5	3.2	5	3.1	2.6	13	4.2	3.5	13.7	3.3	3.5	4.0
n-Undecane	10	9.1	7.3	5.5	19	78	3.6	16	91	19	16	10	28	16	38
Pentylcyclohexane	1.2	0.52	56	1.7	3.0	39	2.7	2.1	19	2.0	2.2	5.4	>1.5	2.2	–
n-Dodecane	>1.7	2.6	–	5.9	12	46	>1.7	8.1	–	9.7	7.9	15	>1.9	7.9	–
TVOC	280	280	0	310	180	38	220	210	3.2	560	270	49	430	270	32
		380[e]	21		299[e]	56		330[e]	28		540[e]	2.6		540[e]	16

[a] Glidden.
[b] Sherwin Williams.
[c] Estimated mass per gram of paint during chamber tests.
[d] Measured concentration measured during bulk product analysis.
[e] Below the method quantitation limit.
[f] Estimated concentration from ASTM methods.

TABLE 2-3. COMPARISON OF DATA FOR CHAMBER EMISSIONS TESTS TO RESULTS FOR BULK PRODUCT ANALYSIS FOR LATEX PAINTS

	SW[a]-Flat (Marmalade) Tests 3 and 4			SW - Gloss (Rose Dawn) Tests 15 and 16			GL[b] - Semigloss (Sea Foam) Tests 17 and 18			SW - Flat (Marmalade)					
										Test 19			Test 20		
Compounds	Me[c] (mg/g)	C_b[d] (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD
1,2-Propanediol	2.6	ND	–	NC	ND	–	79	38	49	1.9	ND	–	2.1	ND	–
Ethylene glycol	37	29	17	60	48	15	45	19	57	25	29	10	30	29	2
2-(2-Butoxyethoxy)ethanol	1.2	1.5	18	25	13	46	11	4.4	60	1.1	1.5	24	1.3	1.5	12
Texanol	14	5.1	66	2.7	27	1	89	5.7	124	14	5.1	66	16	5.1	73
TVOC	49	36	22	88	65	21	140	68	49	34	36	3	41	36	10
		65[e]	20		84[e]	3		93[e]	31		65[e]	44		65[e]	32
Formaldehyde	0.08	NM[f]	–	0.03	NM	–	0.02	NM	–	0.12	NM	–	0.11	NM	–
Acetaldehyde	0.53	NM	–	0.14	NM	–	0.06	NM	–	NC[g]	NM	–	0.21	NM	–

[a] Sherwin Williams.
[b] Glidden.
[c] Estimated mass emitted per gram of paint during chamber tests.
[d] Concentration measured during bulk product analysis.
[e] Estimated concentration from ASTM methods.
[f] Not measured.
[g] Not calculated - curve did not adequately describe the data.

model the emissions. The reason for the very poor agreement between the two measures for Texanol from the latex paints is unknown.

2.4 METALS ANALYSIS

Two methods were evaluated for the analysis of metals in alkyd and latex paints. The first method used X-ray fluorescence spectroscopy (XRF) on untreated liquid paint samples. The second method used inductively coupled plasma emission spectroscopy (ICP) on previously digested paint samples. The XRF method was performed on single aliquots of each of 20 paint samples. The ICP method was performed on triplicate aliquots for the same 20 paint samples to provide data on metal concentrations and method precision.

The ICP method showed acceptable performance in terms of low background contamination in method blanks and good recovery for spiked blanks and spiked paint samples. Variability evaluated as %RSD was generally low (<30%) for most metals measured in replicate samples. For some samples where precision was poor for all metals, high variability appeared to be a result of poor sample homogeneity. For other samples, incomplete digestion may have caused interferences with specific metals in the sample. Performance of the XRF method was not evaluated on this work assignment.

Table 2-4 gives the percentage of samples with measurable concentrations of the target metals. Percent measurable values are provided by manufacturer and paint type as well as for all paint samples. For the metals that were detected, aluminum gave the highest concentrations ranging from 1.5 to 40 mg/g. Concentration results reported by the ICP and XRF methods were not in good agreement and generally differed by a factor of two or more.

TABLE 2-4. PERCENTAGE OF PAINT SAMPLES WITH MEASURABLE CONCENTRATIONS OF METALS

	Quantitative Limit (µg/g)		% Measurable									
			Latex				Alkyd					
			Sherwin Williams		Glidden		Sherwin Williams		Glidden		ALL	
	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF
Aluminum	50[a]	–	100	–	100	—	100	—	100	—	100	—
Selenium	60	2	0	0	20	0	20	0	0	0	0	0
Barium	0.5	50	80	—	80	0	100	0	80	0	90	0
Antimony	40	5	0	0	20	0	40	0	0	0	15	0
Cobalt	10	20	100	0	100	20	100	0	80	0	95	5
Cadmium	1.0	5	0	0	0	0	0	0	0	0	0	0
Arsenic	30	20	0	0	60	0	40	0	40	0	35	0
Chromium	2.0	5	60	40	100	20	100	20	100	40	90	30
Copper	2.0	2	40	100	20	100	20	100	20	100	25	100
Strontium	1.0	—	80	—	100	—	100	—	100	—	95	—
Lead	15	10	20	40	80	80	80	60	0	20	45	50
Manganese	2.0	5	80	20	60	60	80	20	100	20	80	30
Molybdenum	5.0	5	0	0	0	0	0	0	0	100	0	25
Nickel	15	15	0	80	0	40	40	20	0	100	10	60
Mercury	30	10	80	0	60	0	40	80	40	20	55	25
Tin	75	25	0	0	0	0	20	0	0	0	5	0
Zinc	—	1	—	80	—	100	—	100	—	100	—	95
Bismuth	—	5	—	0	—	0	—	0	—	0	—	0
Calcium	—	0.1%	—	100	—	100	—	80	—	20	—	75
Titanium	—	NR[b]	—	100	—	100	—	100	—	100	—	100
Iron	—	NR[b]	—	100	—	100	—	100	—	100	—	100

[a] Not analyzed by test method.
[b] Not reported.

SECTION 3.0
RECOMMENDATIONS

Throughout this work assignment, the methods proposed for testing appeared to work well and provided suitable data for assessing emissions from paint samples. For the small chamber tests, the model fitting process can adequately explain most of the features of the paint emissions, characterizing the analytes in terms of emission factors and decay rates. There are, however, some inadequacies that could be profitably addressed. These are discussed as recommendations below.

1. Placing the painted plates into the chamber sometimes introduces a large quantity of paint vapors. This can be accounted for in the fitting process, but introduces a variable into the measurement that would be better removed. A brief, high volume gas purge of the chamber during and immediately after the plate is set into the chamber would lower any vapor concentration significantly and reduce its impact on the fitting process.
2. Some of the alkyd VOC analyte emissions are not well-defined after 24 hours, particularly those less volatile than n-undecane. If these need better characterization, sampling should be performed at roughly 6-8 hour intervals for the period from 12 hours after application to 48 hours after application.
3. The source models used for the SVOCs and VOCs showing gradual increases in chamber concentrations over time could be better justified. An investigation of different, diffusion-limited emission models might find a physically reasonable model that would better represent the emission rates. It would then give more reliable estimates of the total emissions and the long-time concentrations.
4. Consideration should be given to models that combine a fast-peaking component with a slower-peaking component. The slow-peaking component may not contribute much to the maximum concentration, but does keep the long-time concentration much higher than expected from the fast-peaking model.

SECTION 4.0

LITERATURE SEARCH ON ADDITIONAL OR ALTERNATIVE METHODS

Prior to initiating any experimental work, a review was performed to identify additional or alternative methods for characterizing emissions from IACs that should be evaluated as part of this work assignment. To accomplish this, a computerized literature search was performed to identify published reports or methods for the determination of VOCs, SVOCs, aldehydes, and metals in the liquid IAC products, as well as methods for the measurement of emissions of VOCs, SVOCs, and aldehydes from liquid products. Keywords for the search were determined by reviewing in-house literature on the subject. Keywords included paints, coatings, metals, specific metals (e.g., lead, titanium), aldehydes, formaldehyde, VOCs, SVOCs, and others. A hierarchical search was performed to obtain a manageable list of titles and abstracts to review. Relevant reports were obtained at local libraries or ordered. In-house literature was reviewed, including the ASTM Section 6 volumes on paints and coatings (2). Contacts were also made with researchers in the U.S. who have reported results of these types of tests.

A letter report describing the results of this review was submitted to the EPA Work Assignment Manager (WAM). A copy of this report is given in Appendix A.

SECTION 5.0
PAINT SAMPLES FOR TESTING

5.1 SELECTION AND PROCUREMENT OF PAINT SAMPLES

The IACs tested during the work assignment were limited to latex (water-borne) and alkyd (solvent-borne) paints. Specific paints for testing were selected based on four factors:

- type of paint - alkyd versus latex; within the latex category, a further distinction was made between those based on vinyl acetate and acrylic polymers,
- type of gloss - flat, semi-gloss, or gloss,
- color - a random assortment of colors were obtained in an attempt to represent a wide range of metallic and organic pigments, and
- grade of paint - a medium to high grade, most typical of that purchased for residential applications.

A total of twenty paint samples were selected and purchased for volatile emissions testing and metals analysis. Twelve paints were selected for VOC testing. These twelve plus an additional eight paints were used for metals testing.

Paints for emissions testing were selected to provide a broad range of paint types in order to assure that the tested methods are applicable to a wide variety of paints. The focus of this work assignment was on comparisons between paint types. In order to address differences between alkyd and latex paints and three major gloss types, six different paints were tested. Those selected are shown in Table 5-1. To address differences between manufacturers, paints manufactured by Sherwin-Williams, which has 16% of the market share for architectural coatings (3) and Glidden (13% market share) were selected. Since latex paints based on vinyl acetate copolymers may contain aldehydes, an attempt was made to select vinyl latex paints from each manufacturer. However, vinyl latex paints were available only from Sherwin Williams.

Twelve paints were selected for bulk product analysis by GC/MS, total volatile and water content by the ASTM methods, and small chamber emission tests. These twelve plus an additional eight paints were analyzed by the two metals methods. Paints were selected based on the following criteria:

TABLE 5-1. LIST OF PAINTS SELECTED FOR TESTING

Paint Type[a]	Gloss Type	Manufacturer Series	Color Group	Manufacturer's ID No.	Color Name
SHERWIN WILLIAMS					
Alkyd	Flat	ProMar 200	Yellow	SW1352	Crescent Cream
Alkyd	Semi-gloss	ProMar 200	Blue	SW1529	Violet Veil
Alkyd	Gloss	ProMar 200	Green	SW1435	Bumbershoot
Latex	Flat	ProMar 200	Orange	SW1629	Marmalade
Latex	Semi-gloss	ProMar 200	Purple	SW1545	Vibrant Violet
Latex	Gloss	ProMar 200	Red	SW1604	Rose Dawn
Latex	Flat	ProMar 200	Green	SW1734	Grass Roots
Latex	Semi-gloss	ProMar 200	Other[b]	SW1125	Praline
Alkyd	Flat	ProMar 200	Other	SW1003	First Star
Alkyd	Semi-gloss	ProMar 200	Other	SW1309	Coral Canyon
GLIDDEN					
Alkyd	Flat	5700	Yellow	25312	Chim Cham
Alkyd	Semi-gloss	UH8000	Green	46212	Seafoam
Alkyd	Gloss	4550	Purple	76262	Hyacinth
Latex	Flat	3480	Red	01044	Tomahawk
Latex	Semi-gloss	UH6380	Blue	64984	Down Yonder
Latex	Gloss	6918	Orange	16112	Orange Glaze
Latex	Semi-gloss	UH6300	Blue	64542	Ice Cap
Latex	Gloss	6987	Orange	20573	Orange Ice
Alkyd	Flat	5718	Green	34722	Antigua
Alkyd	Gloss	4550	Other	20852	Sheriff's Star

[a] Paints 1 through 6 of each manufacturer were used for analysis by the ASTM methods, bulk product analysis, metal analysis, and small chamber tests; paints 7 through 10 were used for metals analyses only.

[b] Other refers to paint colors that could not be classified in the basic color groups (i.e., greens, browns).

- Selections included five latex and five alkyd paints manufactured by Glidden and five latex and five alkyd paints manufactured by Sherwin-Williams.
- Selections from Sherwin Williams included two flat, two semi-gloss, and one gloss latex paint and two flat, two semi-gloss, and one gloss alkyd paints.
- Selections from Glidden included one flat, two semi-gloss and two gloss latex paints and two flat, semi-gloss and two gloss alkyd paints.
- The Sherwin Williams latex contained vinyl acetate polymers.
- Paint colors were selected at random after stratification for the six primary color groups (red, orange, yellow, green, blue, red). Manufacturer's color charts were obtained for the paints selected. The color chart was divided into six strata based on primary color group. Each color available within that strata were assigned a sequential number. A random number generator was used to select one color from each strata. This procedure was performed first for the 6 paints from each manufacturer selected for bulk product analysis. Then sequential numbers were assigned to all paint colors on the chart (no stratification by color group) for each manufacturer. Four additional paint colors were selected at random from each manufacturer to obtain the eight additional paints needed for metals analysis.

Medium to high grade paints were selected for testing. The Glidden paints represented "homeowner" used paints. These paints are typically sold in home improvement stores and represent the medium grade paints. The Sherwin Williams paints represented a "top of the line" contractor paint. Selection of this series of paint was based on the availability of all gloss types in the same paint series. The Sherwin Williams series also contained vinyl polymers in the latex paints. Selection of the paint series was made in consultation with the ICF and EPA WAMs.

A final list of the paints selected were provided to the ICF and EPA WAM for approval prior to purchase. Paints were purchased in the Raleigh/Durham, NC area from the company retail outlets. Two gallons of each paint were purchased, one for use in these tests and one to archive. Procedures for collection of product information, such as lot numbers and Material Safety Data Sheets (MSDSs) were performed as in the previous study on IACs performed by RTI (1). Additional information was unavailable from the manufacturer on product color and pigment content.

Additional information pertaining to the paint selection are presented in Appendix B.

5.2 SAMPLE ALIQUOTING

Each one gallon can of paint purchased for testing was divided into a number of small aliquots to be used for all subsequent testing. Individual aliquots were prepared for each test. Generally, an aliquot was used for a single test or analysis and once opened was not used again. For ASTM method 2369 and 4017 the same aliquots were used. By doing this, fresh, unexposed aliquots were available for all tests.

To aliquot each paint sample, a one gallon can of paint was mixed at the store after addition of the color pigments using the store's paint shaker. The paint was then delivered to the laboratory. Immediately prior to aliquoting, the paint sample was again thoroughly mixed by placing it in a rotating mixer and tumbling it end-over-end for at least 1 hour (1620 revolutions). The can was then removed from the mixer, opened, and the paint gently poured directly into a clean, acid washed 2 L glass separatory funnel for dispensing. Vials to be used for aliquoting were cleaned and labeled. Three 6 mm glass beads were placed in each vial as an aid for mixing the sample immediately prior to use. The labeled vials and bottles were then quickly filled with paint and sealed. After aliquoting, the vials were weighed. Aliquots were organized by paint code and aliquot number in boxes and stored protected from light at room temperature until tested. Chain of custody/aliquot tracking forms were prepared for each sample. Examples of these forms are shown in Figures 5-1 and 5-2.

5.3 SAMPLE UNIFORMITY AND STORAGE EFFECTS

The procedures for dispensing and storing the aliquots were designed to provide uniformity between aliquots and to minimize losses of volatile components during storage. In order to assess the uniformity between aliquots, analysis of duplicate aliquots was performed using the ASTM methods D2369 and D4017 for total volatile content and water content respectively. Additionally, the bulk product analysis by GC/MS was performed on duplicate aliquots of one latex flat, latex semigloss, alkyd semigloss, and alkyd gloss paint. Aliquots selected for these analyses were randomly selected and were not sequential aliquots.

CHAIN OF CUSTODY RECORD
ARCHITECTURAL COATINGS STUDY--PROJECT 5522

PAINT ALIQUOT CODE: SW200-1629-LVFO-28
TEST METHOD: ____________________
TEST DATA - NOTEBOOK NO: __________ *PAGES:* ________

	SAMPLE COLLECTION			STORAGE	RECEIVED		SAMPLE ANALYSIS		
SAMPLE CODE:	*MEDIA*	*ID*	*DATE*	*LOCATION*	*ID*	*DATE*	*ID*	*DATE*	*FILE NO.*

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Figure 5-1. Chain of Custody Record

PAINT ALIQUOT TRACKING SHEET
ARCHITECTURAL COATINGS---PROJ. 5522-022

MFG. CODE:	SW	*DATE:*	
MFG. SERIES:	200 (ProMar)	*VOLUME:*	
MFG. ID NO:	1435		
PAINT TYPE:	AD		
GLOSS TYPE:	G		
COLOR GROUP:	G		
MFG. COLOR:	Bumbershoot		
PAINT CODE:	SW200-1435-ADGG		

ALIQUOT VIAL NO.	STORAGE LOCATION	RELINQ. ID	REC'D ID	DATE	TEST METHOD	COMMENTS
-01						
-02						
-03						
-04						
-05						
-06						
-07						
-08						
-09						
-10						
-11						
-12						
-13						
-14						
-15						
-16						
-17						
-18						
-19						
-20						
-21						
-22						
-23						
-24						
-25						
-26						
-27						

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Figure 5-2. Paint Aliquot Tracking Sheet

Effects of storage and sample uniformity after several months of storage were evaluated by repeating the GC/MS bulk product analysis. Also, the weight of each vial measured at the time of aliquoting was compared to the weight at the time of analysis as an indicator of overall aliquot integrity.

SECTION 6.0
ASTM METHOD

6.1 OVERVIEW

The ASTM Methods D2369 and D4017 were performed on the 12 paint samples designated in Table 5-1 to determine total volatile content and water content, respectively. Method D2369 is a gravimetric method; D4017 is the Karl Fischer titration method for water determination. The methods are described in the ASTM Volume 6.01 (4). As discussed in Section 5, paints selected for testing on this work assignment were mixed, then aliquotted into small glass jars and stored for all subsequent testing (ASTM methods, bulk analysis, small chamber tests). To evaluate sample uniformity between jars, measurements using the ASTM methods were performed on samples taken from duplicate jars. In addition, measurements were made on duplicate samples taken from each jar to obtain data on method precision.

6.2 METHODS

The ASTM Standard Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings, ASTM D3960-91 (ASTM D3960-91 (2) describes the tests used in this study for determination of VOC and water content in the paints.

The ASTM Standard Test Method for Volatile Content of Coatings, ASTM D2369-90, (4) was followed for the gravimetric determination of the volatile content. To perform the test, the paint was drawn into a disposable 3-mL syringe, which was then weighed. Approximately 0.5 grams of paint was dispensed into a tared aluminum weighing pan. The syringe was then re-weighed to determine the exact mass dispensed into the pan. This technique minimized loss of volatile components during preparation of the test samples. The samples were dried at 112°C for 60 minutes. The pan with the paint sample was re-weighed to determine the mass of solids remaining. The percent volatile content was determined by difference. Two blank samples consisting of empty aluminum weighing pans were also weighed and dried. The differences between the pre- and post-drying weights of the blanks were less than 0.0003 g.

The water content of the paint samples was determined according to the ASTM Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method, ASTM D4017-90 (5). The instrument used was a Fisher Coulomatic K-F Titrimeter (Model 447, Fisher Scientific, Pittsburgh, PA). This model determines moisture content of samples by automatic titration with coulometrically generated Karl Fischer reagent (Coulomat A and Coulomat C - both pyridine free).

6.3 RESULTS

Results for the ASTM test are given in Table 6-1 for % nonvolatile, % volatile, and % water content. Calculated % TVOC values for each sample are also provided. This estimate was made for each sample by subtracting the mean % water content from the mean % volatiles content. For all measures, the mean paint content as well as the % RSD for replicate analyses and replicate aliquots are provided. Results show excellent precision (i.e., low % RSD values) for all measures both within and between samples, indicating both good method precision and sample uniformity. Highest % RSD values (1.4 to 16) were calculated for % water content of alkyd paints. This is expected since the water content of these paints is so low (i.e., >1%).

TABLE 6-1. RESULTS OF ASTM TESTS ON PAINT SAMPLES

	% Nonvolatiles[a]				% Water[b]			
Paint Type	Mean[a]	Mean % RSD for Replicate Analysis	% RSD for Replicate Aliquots	% Volatiles[a]	Mean	Mean % RSD for Replicate Analysis	% RSD for Replicate Aliquots	% TVOC[c]
SHERWIN WILLIAMS								
• Latex								
- Flat (Marmalade)	44.20	0.30[d]	0.52	55.8	49.23	0.64	0.93	6.6
- Gloss (Rose Dawn)	44.14	0.09	0.18	55.9	47.51	2.0	2.22	8.4
- Semigloss (Vibrant Violet)	41.53	0.15	0.32	58.5	51.60	0.96	0.79	6.9
• Alkyd								
- Flat (Crescent Cream)	69.20	0.16	0.16	30.8	0.26	6.14	6.01	30.5
- Gloss (Bumbershoot)	45.75	0.10	0.21	54.3	0.60	2.35	9.52	53.7
- Semigloss (Violet Veil)	61.03	0.28		39.0	0.15	1.58	1.45	38.8
GLIDDEN								
• Latex								
- Flat (Tomahawk)	42.89	0.24	0.20	57.1	53.52	0.64	1.31	3.6
- Gloss (Orange Glaze)	45.64	0.67	0.87	54.4	45.32	1.72	1.66	9.0
- Semigloss (Down Yonder)	36.71	0.40	0.35	63.3	54.02	0.23	0.68	9.3
• Alkyd								
- Flat (Chim Cham)	69.70	0.11	0.16	30.3	0.33	6.26	8.18	30.0
- Gloss (Hyacinth)	61.02	0.19	0.31	39.0	0.85	5.69	5.32	38.1
- Semigloss (Seafoam)	66.41	0.22	0.58	33.6	0.50	6.75	16.28	33.1

[a]Measured using ASTM method D269-90
[b]Measured using ASTM method D4017-90
[c]Calculated as % volatiles - % water
[d]n = 4

SECTION 7.0
BULK PRODUCT ANALYSIS

7.1 OVERVIEW

Bulk product analysis is performed by diluting the paint sample with an appropriate solvent then analyzing the resulting solution by GC/MS to identify and quantify organic components. The method should provide information on the identity and concentration of individual VOCs/SVOCs as well as the TVOC concentration in paint samples. Results of analysis should also identify the VOCs/SVOCs that are likely to occur in emissions from paint samples and may also predict emission rates for these compounds.

In our preliminary study (1), the alkyd paint was diluted with n-hexane and the latex paint was diluted with a solution of 20% water/80% methanol. n-Hexane was an appropriate solvent for diluting the alkyd paint, except that the calculation of TVOC concentrations could not be made by integrating the total ion chromatogram beginning with hexane, as is done for air samples. For latex paints, the use of water/methanol for diluting the latex paint may have resulted in some polymerization of the organic paint components. To overcome these problems, methods for preparing the samples for bulk product analysis were further refined and evaluated on this study. Modifications included a change in dilution solvents and improved methods for removing solids from the diluted samples.

During testing, bulk product analysis was performed on six paints (latex flat, latex semigloss, latex gloss, alkyd flat, alkyd semigloss, and alkyd gloss) manufactured by Sherwin Williams and a comparable set of six paints manufactured by Glidden. The identity of these paint samples is given in Table 5-1. The first analysis was performed to identify the eight most abundant VOCs/SVOCs in the twelve paints. Reference standards were then procured, calibration standards prepared at multiple concentration levels, and quantitative analysis performed.

For four of the paints (e.g., Sherwin Williams latex flat, Glidden latex semigloss, Glidden alkyd semigloss, and Sherwin Williams alkyd gloss), duplicate paint aliquots (paint samples taken from separate vials) were diluted and analyzed to determine method precision. A single aliquot of the other eight paints was analyzed to obtain data on the major analytes in the paints.

Results of the proposed tests were intended to provide data on the appropriate dilution solvents, the precision of the method, and the composition of six different types of paints formulated by two different manufacturers.

7.2 METHODS

7.2.1 Sample Preparation

Paint samples for the bulk product analysis were prepared by diluting a known weight of paint, either alkyd or latex, to a fixed volume using a suitable solvent. All alkyd paints were diluted in n-pentane and all latex paints were diluted in acetone. Prior to aliquoting the paints for testing, sample vials containing the paint were first shaken then vortex mixed for 60 seconds to assure the thorough mixing of the paint within the vial. A pipette was used to transfer paint directly into a clean, tared 15 mL graduated centrifuge tube. The centrifuge tube containing paint was then weighed. The amount of paint (P_A) transferred to the tube was calculated as

$$P_A = W_{Ta} - W_{Tb} \qquad (7\text{-}1)$$

where W_{Ta} and W_{Tb} are the weights of the tube after and before paint was added. The sample was immediately diluted to volume (10 mL) using the appropriate solvent and spiked with a known amount of external quantitation standard. The tube containing the diluted sample was sealed and vortex mixed for approximately 30 seconds. To facilitate the removal of particulates and polymers from the sample prior to GC/MS analysis, the samples were centrifuged approximately five minutes. For analysis a small aliquot of the supernate was transferred to an autosampler vial for subsequent analysis by GC/MS. Aliquots for analysis were diluted as necessary so the sample concentrations fell within the calibration range.

7.2.2 GC/MS Analysis

Samples of paints diluted in solvents were analyzed by direct injection (1 µL) onto the GC column. Operating parameters for the GC/MS system are listed in Table 7-1. Target analytes for quantitation were identified based on an electronic database search of the NIH/EPA/MSDC Mass Spectral Data Base and the Registry of Mass Spectral Data (7).

During quantitative analyses, identification of target analytes was based on chromatographic retention times relative to the external standard and on relative

TABLE 7-1. OPERATING PARAMETERS FOR THE CAPILLARY GC/MS SYSTEM

Parameter	Setting
GAS CHROMATOGRAPH	
Instrument	Hewlett-Packard 5890
Column	30m x 0.32mm DB-624 widebore fused silica capillary column
Temperature Program	35°C (5 min) to 250°C (5 min) @ 5°C/min
Carrier Gas Flow Rate	1.98 mL/min
Capillary injector	1 min splitless
Injector temperature	200°C
MASS SPECTROMETER	
Instrument	Hewlett Packard, Model 5988A
Ionization Mode	Electron Ionization
	Scan 25 - 350 m/z
Emission Current	0.3 mA
Source Temperature	200°C
Electron Multiplier	2000 volts[a]

[a]Typical value.

abundances of the extracted ion fragments selected for quantitation. Fragment ions were selected based on mass spectra acquired during qualitative analysis and historical data.

Quantitation of VOCs/SVOCs was accomplished using chromatographic peak areas derived from extracted ion profiles. Specifically, relative response factors (RRFs) for each target compound were generated from the analysis of standard solutions (Tables 7-2 and 7-3) prepared at five different concentrations. For each standard, RRFs were calculated as:

$$RRF_T = \frac{A_T \cdot C_{QS}(ng/\mu L)}{A_{QS} \cdot C_T(ng/\mu L)} \tag{7-2}$$

where A_T is the peak area of the quantitation ion for the target VOC/SVOC and A_{QS} is the peak area of the external standard. C_T is the concentration of target compound in the calibration standard and C_{QS} is the concentration of the external standard in the calibration standard sample.

Because the calibration standards encompassed such a wide concentration range, the instrumental response for many of the target analytes was not linear over the entire range. For the alkyd paint standards both the response of the external quantitation standard and the target analytes decrease substantially at the higher concentrations. Only the low level standards (5 to 280 ng/µL) were used for quantitation and samples were diluted so that concentrations did not exceed the concentrations of the highest quantitation standard. Where instrumental linearity was not demonstrated, the standards used to quantitate a specific analyte (shown in Table 7-2 and 7-3) were selected to bracket the concentration of that analyte found in the diluted paint samples. Using these standards, mean values and standard deviations of the RRFs were calculated for each target analyte. For the calibration to be considered acceptable, the mean RRF value had to be defined by at least three calibration standards that bracketed the sample concentrations and the RSD of the calculated RRF had to be less than 30%. During each day of analysis, an additional standard was analyzed. If the RRF values for this standard were within ±25% of the RRFs for the same concentration standard obtained during calibration, the GC/MS system was considered "in control" and the mean RRF values from the calibration standards were used to calculate the concentration of the target VOCs in sample extracts (C_{EX}) as:

TABLE 7-2. CALIBRATION SOLUTIONS FOR BULK PRODUCT ANALYSIS OF ALKYD PAINTS

Compound	Concentration (ng/µl) in Pentane[a]						
ANALYTES							
o-Xylene	5.00	28.0	52.0	104	256	500	2518
m-Xylene	4.99	27.9	51.9	104	256	499	2515
p-Xylene	4.98	27.9	51.8	104	255	498	2510
Propylcyclohexane	4.96	27.8	51.5	103	254	496	2498
1,3,5-Trimethylbenzene	4.97	27.8	51.7	103	254	497	2504
1,2,3-Trimethylbenzene	4.92	27.5	51.1	102	252	492	2478
1,2,4-Trimethylbenzene	4.89	27.4	50.9	102	250	489	2464
2-Methyldecane	4.61	25.8	47.9	95.8	236	461	2322
n-Nonane	4.49	25.1	46.7	93.3	230	449	2262
n-Decane	4.56	25.6	47.5	94.9	234	456	2300
trans-Decahydronaphthalene	5.00	28.0	52.0	104	256	500	2521
n-Undecane	4.63	25.9	48.1	96.2	237	463	2331
Pentylcyclohexane	4.82	27.0	50.2	100	247	482	2431
n-Dodecane	4.69	26.3	48.8	97.5	240	469	2363
2-Ethyltoluene	4.88	27.3	50.7	101	250	488	2459
3-Ethyltoluene	4.97	27.9	51.7	103	255	497	2507
4-Ethyltoluene	4.95	27.7	51.5	103	253	495	2495
1,1-Dimethylcyclohexane	4.86	27.2	50.5	101	249	486	2448
Toluene	4.99	27.9	51.8	104	255	499	2513
EXTERNAL QUANTITATION STANDARD							
Bromopentaflurobenzene	200	200	200	200	200	200	200

[a]Shaded standard used for instrument calibration.

TABLE 7-3. CALIBRATION SOLUTIONS FOR BULK PRODUCT ANALYSIS OF LATEX PAINTS

Compound	Concentration (ng/µl) in Acetone[a]							
ANALYTES								
2-Methyl-2-propanol	24.1	49.8	99.6	251	498	996	2490	4980
Ethylene glycol	24.2	50.0	99.9	251	500	999	2498	4995
1,2-Propanediol	23.9	49.2	98.5	248[b]	492	985	2462	4923
o-Xylene	24.2	49.9	99.8	251	499	998	2495	4990
m-Xylene	24.2	49.8	99.7	251	498	997	2492	4984
p-Xylene	24.1	49.7	99.5	250	497	995	2486	4973
n-Butyl ether (dibutyl ether)	24.0	49.4	98.8	249	494	988	2471	4942
Methyl sulfoxide	24.3	50.1	100	252	501	1003	2507	5014
n-Propylbenzene	24.0	49.5	99.0	249	495	990	2475	4950
1,2,3-Trimethylbenzene	24.0	49.6	99.1	249	496	991	2478	4956
1,2,4-Trimethylbenzene	23.9	49.3	98.6	248	493	986	2464	4929
1,3,5-Trimethylbenzene	24.1	49.6	99.2	250	496	992	2481	4961
2-(2-Methoxyethoxy)ethanol	24.2	50.0	100	251	500	1000	2500	5000
2-Ethyltoluene	23.8	49.2	98.4	247	492	984	2459	4918
3-Ethyltoluene	24.1	49.7	99.3	250	497	993	2483	4967
4-Ethyltoluene	24.0	49.4	98.9	249	494	989	2472	4944
Diethylene glycol	24.3	50.2	100	252	502	1004	2509	5018
Dipropylene glycol	23.6	48.6	97.2	245	486	972	2431	4861
2-(2-Butoxyethoxy)ethanol	24.1	49.8	99.6	250	498	996	2489	4978
2-(2-Butoxyethoxy)ethyl acetate	24.4	50.3	101	253	503	1007	2517	5035
Dimethoxymethane	23.9	49.4	98.8	248	494	988	2469	4938
Texanol	26.7	55.0	110	277	550	1100	2749	5498
INTERNAL STANDARD								
n-Octanol	198	198	198	198	198	198	198	198

[a]Shaded standards used for instrumental calibration.
[b]Used for single point quantitation.

$$C_{EX}(ng/\mu L) = \frac{A_T \cdot C_{QS}(ng/\mu L)}{A_{QS} \cdot RRF_T} \tag{7-3}$$

The concentrations of the analytes in the paint sample were then adjusted for the dilution factor and weight of paint diluted as:

$$C(mg/g) = \frac{C_{EX}(ng/\mu L) \cdot 10{,}000\ \mu L}{W(g) \cdot 1000} \tag{7-4}$$

where W is the weight (grams) of the paint.

For alkyd paints, TVOCs were calculated from the reconstructed ion chromatogram (RIC). The total area of the RIC was integrated for the retention time window from n-hexane through n-tetradecane. The TVOC concentration was calculated based on the average total ion response factor generated for toluene. Since the only compounds in the latex paints were target analytes, TVOCs for these samples were calculated by summing the measured concentrations of the individual targets.

7.3 RESULTS

7.3.1 Qualitative Identification

Organic constituents identified during bulk analysis of alkyd and latex paints are given in Tables 7-4 and 7-5 respectively. GC/MS total ion chromatograms for these analyses are provided in Figures 7-1 to 7-4. As seen in Figures 7-1 and 7-2, the alkyd paints contain hundreds of compounds that are predominately branched chained hydrocarbons. The compounds identified in these paint samples represent the most abundant VOCs where probable isomeric identification could be made. A visual comparison of the chromatograms for the alkyd paints shows a higher relative abundance of the more volatile species for the semigloss and gloss finishes compared to the flat finishes.

In contrast, the latex paints contain relatively few volatile organic chemicals. The VOCs identified during analysis generally account for all of the components in the GC/MS chromatograms. For the various paint samples tested, the presence and relative abundance

TABLE 7-4. IDENTIFICATION OF MAJOR CHROMATOGRAPHIC PEAKS IN ALKYD PAINT SAMPLES

	Paint Sample[a]					
	Gloss		Semigloss		Flat	
Compound	Sherman Williams (Bumbershoot)	Glidden (Hyacinth)	Sherman Williams (Violet Veil)	Glidden (Sea Foam)	Sherman Williams (Crescent Cream)	Glidden (Chim Cham)
Xylene isomers	X	X	X	X	X	X
Propylcyclohexane	X	X	X	X		
3- or 4- Ethyltoluene		X		X		
n-Decane	X	X	X	X		X
Trimethylbenzene isomers		X	X	X		
2-Methyldecane	X			X	X	
Decahydronaphthalene	X	X	X	X	X	X
n-Undecane	X	X	X	X	X	X
Pentylcyclohexane					X	X
n-Dodecane	X	X	X	X	X	X

[a] Compounds indicated are those compounds that were at the highest abundance in each sample.

TABLE 7-5. IDENTIFICATION OF MAJOR CHROMATOGRAPHIC PEAKS IN LATEX PAINT SAMPLES

	Paint Sample[a]					
	Gloss		Semigloss		Flat	
Compound	Sherman Williams (Rose Dawn)	Glidden (Orange Glaze)	Sherwin Williams (Vibrant Violet)	Glidden (Down Yonder)	Sherwin Williams (Marmalade)	Glidden (Tomahawk)
2-Methyl-2-propanol			X			
Ethylene glycol	X	X	X	X	X	X
1,2-Propanediol (propylene glycol)			X	X	X	
Xylene isomers				X		
n-Butyl ether			X			
Methyl sulfoxide		X				
n-Propylbenzene		X				
Trimethylbenzene isomers		X				
2-(2-Methoxyethoxy)ethanol		X				
Diethylene glycol	X		X		X	
Dipropylene glycol					X	
2-(2-Butoxyethoxy)ethanol	X	X	X	X	X	X
2-(2-Butoxyethoxy)ethyl acetate				X		X
Texanol	X	X	X	X	X	

[a]Major compounds identified in each sample are identified with an X.

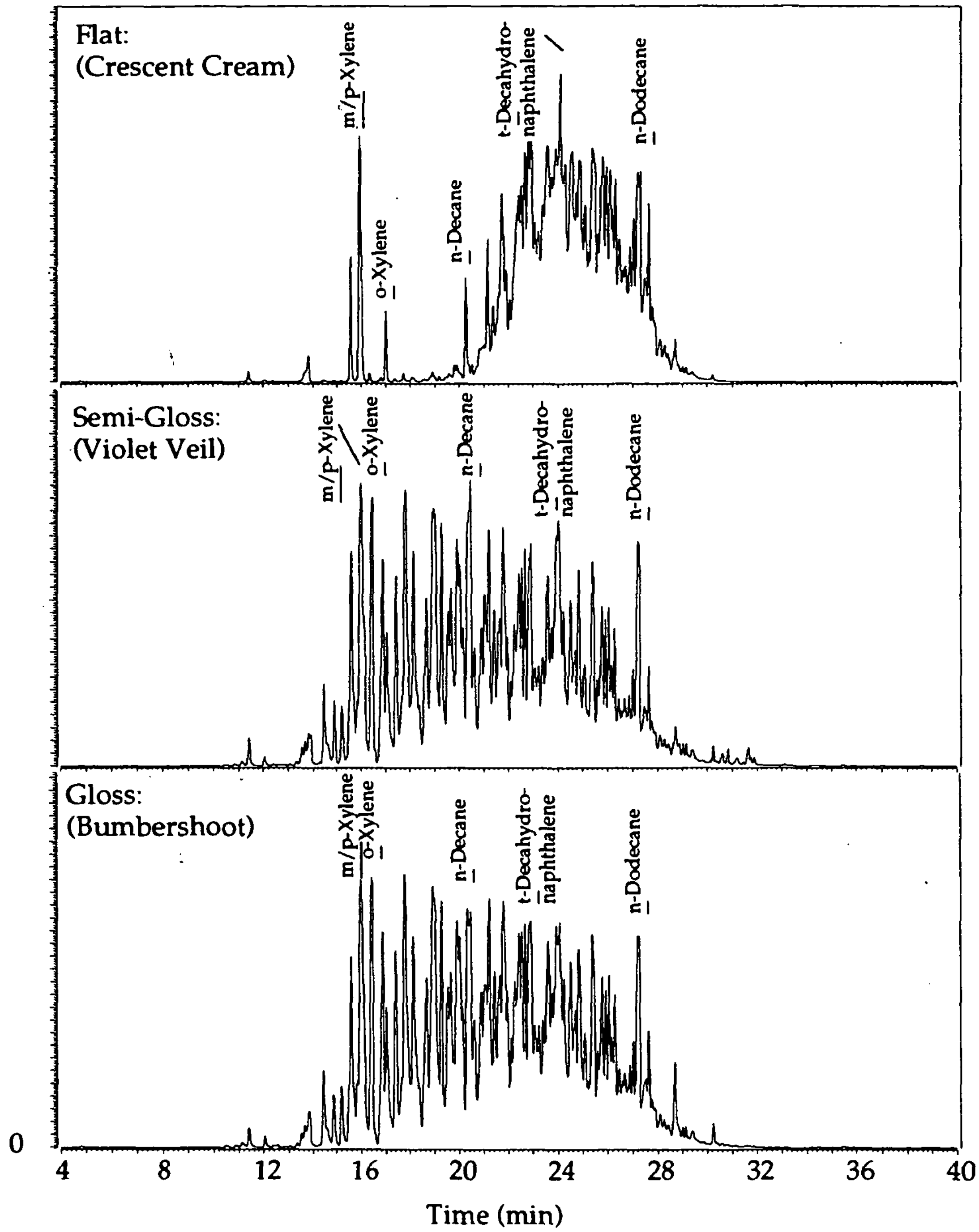

Figure 7-1. Total ion chromatograms of Sherwin Williams Alkyl Paint Bulk Samples (representative compounds indicated on chromatogram).

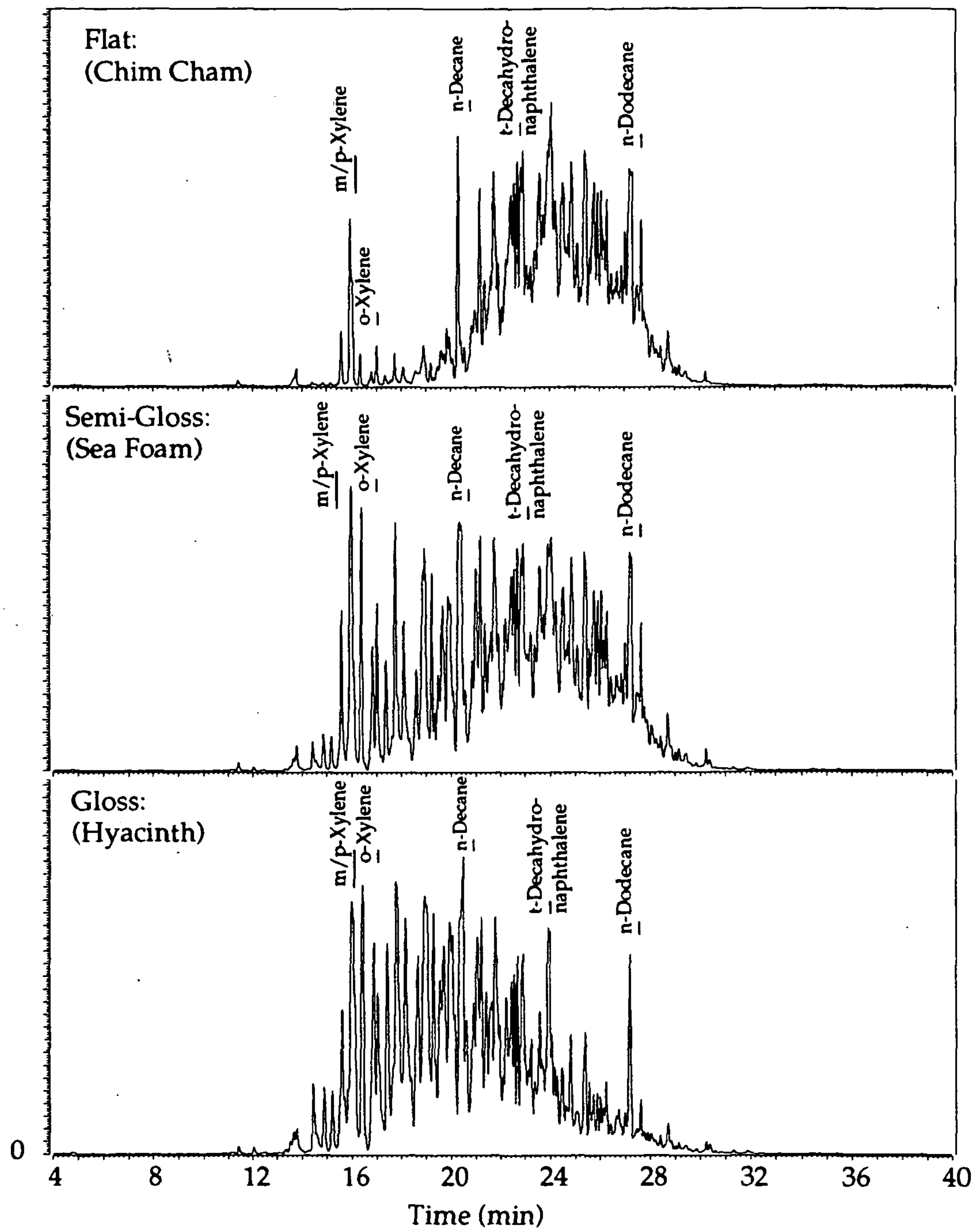

Figure 7-2. Total ion chromatograms of Glidden Alkyl Paint Bulk Samples (representative compounds indicated on chromatogram).

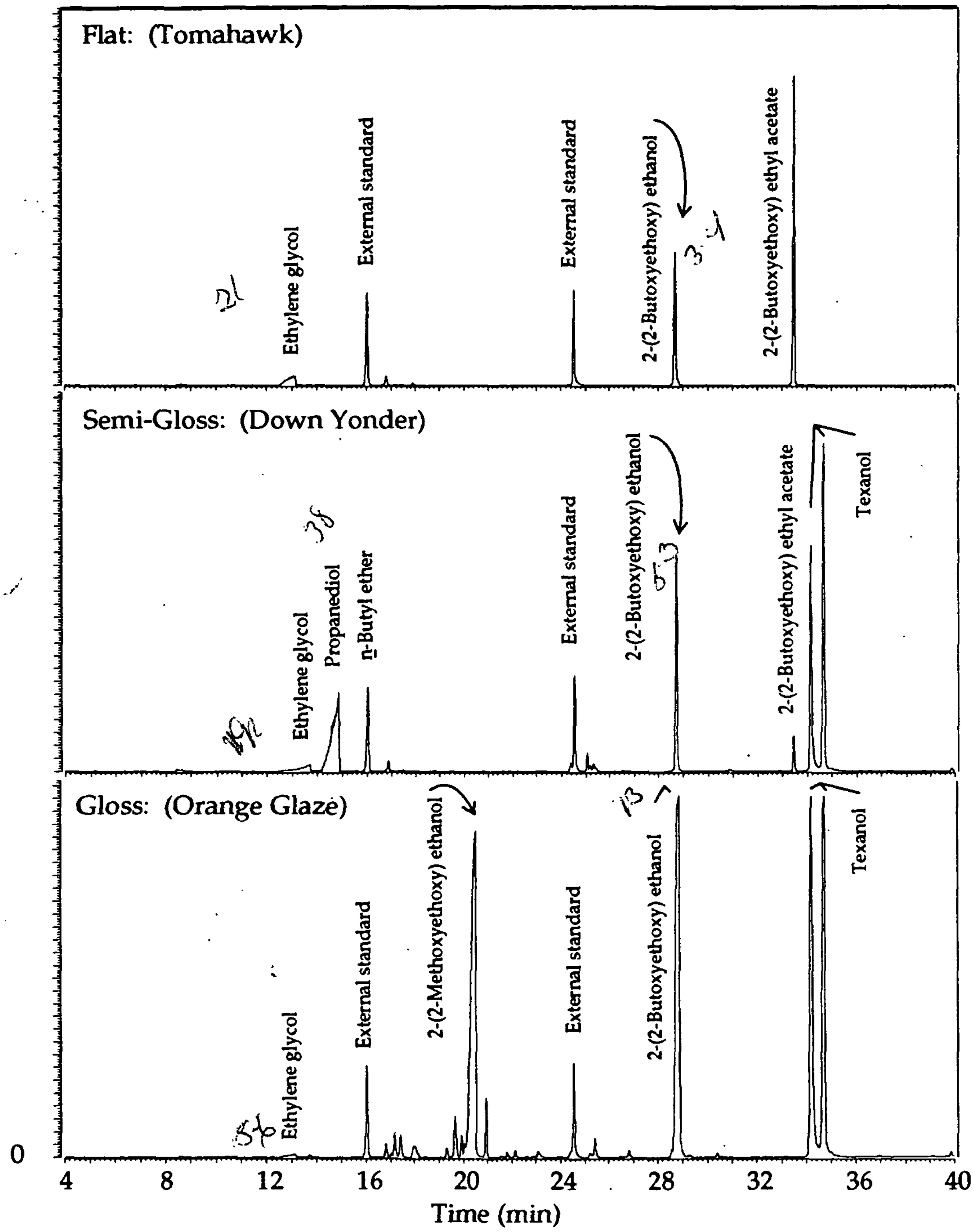

Figure 7-3. Total ion chromatograms of Glidden Latex Paint Bulk Samples.

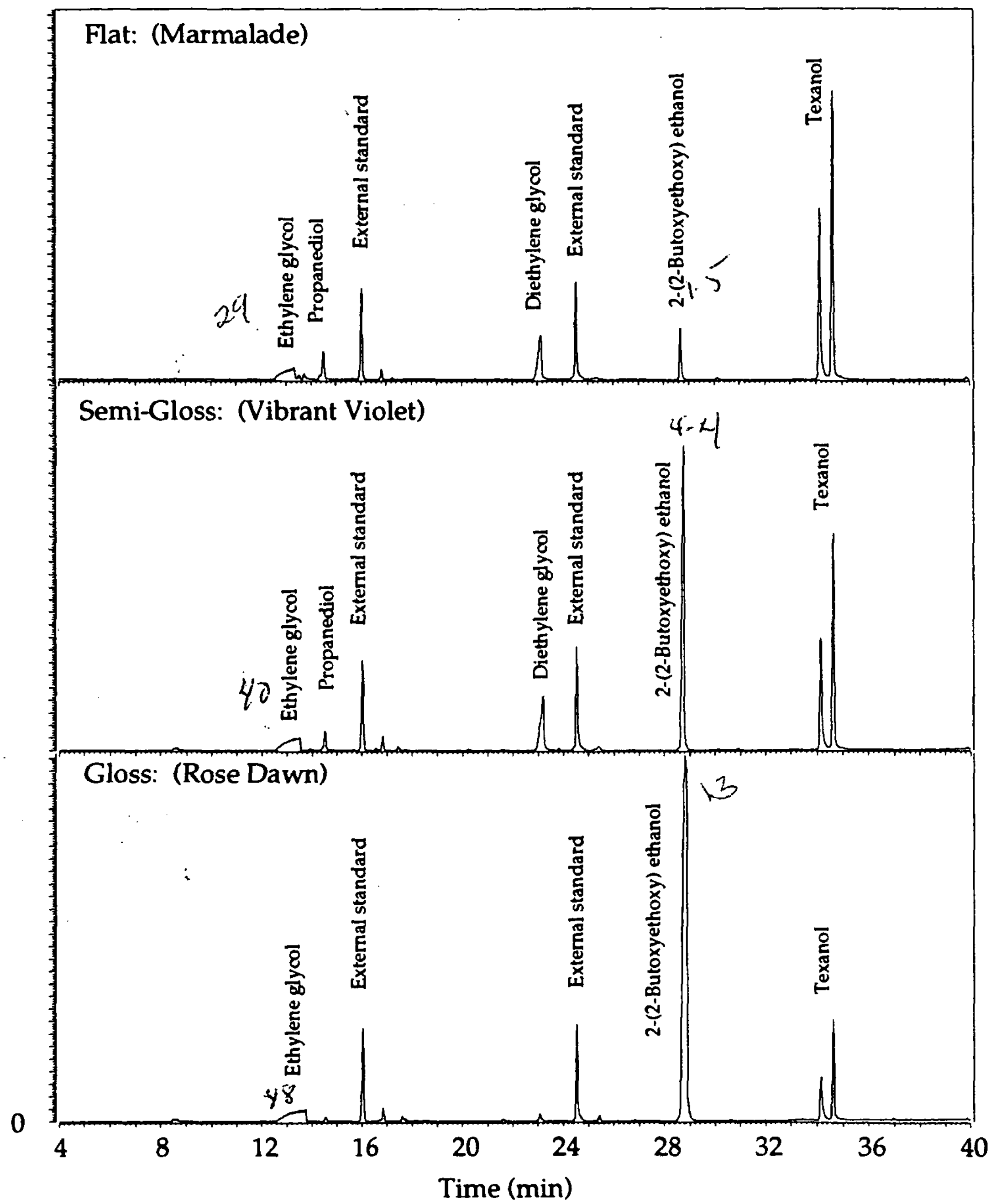

Figure 7-4. Total ion chromatograms of Sherwin Williams Latex Paint Bulk Samples.

of individual VOCs varied between samples with no clear trend for manufacturer or gloss type.

7.3.2 Quantitative Analyses

Results of quantitative analysis for the alkyd paint samples are given in Table 7-6. Similar results are provided for the latex paints in Table 7-7. For the gloss and semigloss alkyd paints, n-nonane, n-decane, n-undecane, n-dodecane, and propylcyclohexane were among the most abundant compounds. For the flat alkyd paint, the most abundant compounds are n-undecane, n-dodecane, and n-decane. For four of the six latex paints, ethylene glycol was the most abundant compound. 1,2-Propanediol and 2-(2-methoxyethoxy)ethanol had the highest concentrations in the other two paint samples. Other compounds with relatively high concentrations (>10 mg/g) included 2-(2-butoxyethoxy)ethanol and Texanol.

Duplicate sample aliquots were analyzed for selected paint samples as a way to assess uniformity of the sample aliquots as well as overall method precision. The %RSD values for these duplicate samples are given in Tables 7-8 and 7-9 for alkyd and latex paint samples, respectively. Results show low %RSD values (generally less than 10%) for both paint types. These data suggest that both the replicate sample aliquots are uniform and the precision of the overall method is good.

Method controls were prepared and analyzed as a further evaluation of method performance. Method controls were dilution solvent spiked with target chemical and external quantitation standards which were then handled and analyzed in a manner identical to paint samples. Nominal spiking levels were equivalent to 1 mg/g of paint. Results for these analyses (Table 7-10) for the alkyd paints show good recovery (82 to 99%) and precision for the paint samples extracted prior to storage. Recovery of method controls prepared and analyzed for the storage stability study (T=29 weeks) were uniformly low (60 to 62%). This could be due to a systematic error (i.e., external quantitation standard spiked to high). However, no reason for this result could be documented. Precision evaluated as the standard deviation of replicate analysis was very good (generally less than 5%) for both sets of method controls. For the latex paint controls (Table 7-11), the recoveries for the initial study were reasonable although somewhat high. 1,2-Propanediol gave a low recovery (45%). However this compound was spiked at a level below the method quantitation limit. The reported recovery is probably a result of a lower GC/MS response for lower concentrations of this

TABLE 7-6. QUANTITATIVE RESULTS FOR TARGET VOCS IN ALKYD PAINT SAMPLES

	Concentration (mg/g)						
	Gloss		Semigloss		Flat		
Compound	Sherwin Williams[a] (Bumbershoot)	Glidden (Hyacinth)	Sherwin Williams (Violet Veil)	Glidden[a] (Sea Foam)	Sherwin Williams (Crescent Cream	Glidden (Chim Cham)	MQL[c] (mg/g)
m,p-Xylene	4.29	3.58	5.14	3.97	2.78	1.56	0.558
n-Nonane	11.2	9.82	9.76	5.32	0.164	0.675	0.279
o-Xylene	0.828	1.06	0.781	1.08	0.565	0.367	0.280
Propylcyclohexane	3.40	4.19	3.24	1.45	ND	0.196	0.278
3- & 4-Ethyltoluene	ND[b]	1.82	0.694	1.30	ND	ND	0.556
1,3,5-Trimethylbenzene	ND	0.788	0.322	0.520	ND	ND	0.278
n-Decane	19.3	18.0	15.9	14.1	1.33	4.51	0.256
2-Ethyltoluene	ND	0.617	ND	0.483	ND	ND	0.273
1,2,4-Trimethylbenzene	0.533	2.76	0.854	1.81	ND	ND	0.274
1,2,3-Trimethylbenzene	ND	0.839	ND	0.635	ND	ND	0.275
2-Methyldecane	3.24	1.98	2.49	2.63	2.97	3.24	0.258
trans-Decahydronaphthalene	3.46	2.10	2.54	2.58	3.49	3.24	0.280
n-Undecane	16.2	9.11	14.0	16.2	18.3	19.1	0.259
Pentylcyclohexane	2.16	0.518	1.54	2.06	3.73	3.01	0.270
n-Dodecane	7.88	2.60	6.89	8.10	11.0	11.5	0.263
TVOC	274	284	314	207	202	179	—

[a] Mean of Duplicate Analysis
[b] Not detected, below MQL
[c] Method Quantitation Limit estimated as the paint concentration that would be equivalent to lowest concentration calibration standard and 1 gram of paint.

TABLE 7-7. QUANTITATIVE RESULTS FOR TARGET SVOCS IN LATEX PAINT SAMPLES

Compound	Concentration (mg/g)						
	Gloss		Semigloss		Flat		
	Sherman Williams (Rose Dawn)	Glidden (Orange Glaze)	Sherman Williams (Vibrant Violet)	Glidden[a] (Down Yonder)	Sherman Williams[a] (Marmalade)	Glidden (Tomahawk)	MQL[c] (mg/g)
2-Methyl-2-propanol	0.36	ND	0.307	ND	ND	ND	0.241
Ethylene glycol	48	5.61	40.1	19.1	29.0	20.8	5.00
1,2-Propanediol	ND[b]	ND	ND	38.3	1.64[d]	ND	10.0
m,p-Xylene	ND	ND	ND	ND	ND	ND	0.483
n-Butyl ether	ND	ND	ND	ND	ND	ND	0.240
o-Xylene	ND	ND	ND	ND	ND	ND	0.242
Methyl sulfoxide	ND	0.889	ND	ND	ND	ND	0.243
n-Propyl benzene	ND	ND	ND	ND	ND	ND	0.240
1,3,5-Trimethylbenzene	ND	ND	ND	ND	ND	ND	0.241
2-(2-Methoxyethoxy)ethanol	ND	22.9	ND	ND	ND	ND	0.242
1,2,4-Trimethylbenzene	ND	0.569	ND	ND	ND	ND	0.240
1,2,3-Trimethylbenzene	ND	ND	ND	ND	ND	ND	0.239
Diethylene glycol	0.62	ND	6.50	ND	5.14	ND	0.243
Dipropylene glycol	ND	0.993	0.392	1.23	0.347	ND	0.236
2-(2-Butoxyethoxy)ethanol	13.0	13.0	5.35	4.42	1.54	3.40	0.241
2-(2-Butoxyethoxy)ethyl acetate	ND	ND	ND	0.498	ND	4.43	0.244
Texanol	2.7	10.5[e]	4.22	5.72	5.13	ND	0.267
TVOC	64.7	54.5	56.9	69.3	41.2	28.6	—

[a] Mean of Duplicate Aliquots.
[b] Not detected: below MQL.
[c] Method Quantitation Limit estimated as the paint concentration that would be equivalent to the lowest concentration calibration standard and 1 gram of paint.
[d] Curve was not linear at lower concentrations, quantitated using a single point calibration.
[e] Greater than 10% above the highest concentration standard.

TABLE 7-8. PRECISION OF BULK ANALYSIS METHOD FOR ALKYD PAINTS

Compounds	% RSD of Duplicates[a] Semigloss Glidden (Sea Foam)	Gloss Sherwin Williams (Bumbershoot)
m,p-Xylene	5.3	5.2
n-Nonane	2.7	1.2
o-Xylene	4.0	1.7
Propylcyclohexane	0.093	0.62
3- & 4-Ethyl toluene	5.2	NC
1,3,5-Trimethylbenzene	1.7	NC
n-Decane	2.2	1.8
2-Ethyl toluene	4.6	NC
1,2,4-Trimethylbenzene	0.36	0.36
1,2,3-Trimethylbenzene	3.0	NC
2-Methyldecane	0.73	2.9
trans-Decahydronaphthalene	1.2	4.4
n-Undecane	1.2	1.4
Pentylcyclohexane	0.56	6.4
n-Dodecane	0.18	4.7
TVOC	12	6.7

[a]% Relative Standard Deviation.
[b]Not calculated, not found in sample above the MQL.

TABLE 7-9. PRECISION OF BULK ANALYSIS METHOD FOR LATEX PAINT

	% RSD of Duplicates[a]	
Compound	Semigloss Glidden (Down Yonder)	Flat Sherwin Williams (Marmalade)
2-Methyl-2-propanol	NC[b]	NC
Ethylene glycol	0.52	7.7
1,2-Propanediol	1.4	NC
m,p-Xylene	NC	NC
n-Butyl ether	NC	NC
o-Xylene	NC	NC
Methyl sulfoxide	NC	NC
n-Propyl benzene	NC	NC
1,3,5-Trimethylbenzene	NC	NC
2-(2-Methoxyethoxy)ethanol	NC	NC
1,2,4-Trimethylbenzene	NC	NC
1,2,3-Trimethylbenzene	NC	NC
Diethylene glycol	NC	4.0
Dipropylene glycol	1.6	6.1
2-(2-Butoxyethoxy)ethanol	0.19	2.7
2-(2-Butoxyethoxy)ethyl acetate	0.28	NC
Texanol	0.93	1.2
TVOC	0.60	6.0

[a]% Relative Standard Deviation.
[b]Not calculated, not found in sample above the MQL.

TABLE 7-10. RESULTS OF METHOD CONTROLS FOR BULK PRODUCT ANALYSIS OF ALKYD PAINT

Compounds	Spike Level (mg/g)	% Recovery ± S.D. Initial Study (n=2)	% Recovery ± S.D. Storage Study (n=2)
m,p-Xylene	2.07	87 ± 2.1	64 ± 0.57
n-Nonane	0.93	93 ± 2.5	60 ± 0.11
o-Xylene	1.04	82 ± 0.54	61 ± 0.78
Propylcyclohexane	1.03	92 ± 1.9	60 ± 0.42
3- & 4-Ethyl toluene	2.06	95 ± 1.2	62 ± 0.27
1,3,5-Trimethylbenzene	1.03	92 ± 3.6	60 ± 0.51
n-Decane	0.95	96 ± 3.0	60 ± 0.33
2-Ethyl toluene	1.02	93 ± 2.4	61 ± 0.10
1,2,4-Trimethylbenzene	1.02	96 ± 1.7	63 ± 0.18
1,2,3-Trimethylbenzene	1.02	96 ± 0.21	61 ± 0.26
2-Methyldecane	0.96	102 ± 3.4	63 ± 0.12
trans-Decahydronaphthalene	1.04	98 ± 1.0	64 ± 1.3
n-Undecane	0.96	97 ± 1.5	61 ± 0.60
Pentylcyclohexane	1.00	99 ± 4.6	60 ± 0.010
n-Dodecane	0.98	95 ± 3.0	62 ± 1.0

TABLE 7-11. RESULTS OF METHOD CONTROLS FOR BULK PRODUCT ANALYSIS OF LATEX PAINT

Compound	Spike Level (mg/g)	% Recovery ± S.D. Initial Study (n = 2)	% Recovery ± S.D. Storage Study (n = 2)
2-Methyl-2-propanol	1.00	116 ± 3.6	146 ± 8
Ethylene glycol	1.00[a]	89 ± 3.5	77 ± 5.5
1,2-Propanediol	0.99[a]	45 ± 3.5	88 ± 4.5
m,p-Xylene[b]	2.00	141 ± 2.8	171 ± 12
n-Butyl ether[b]	0.99	122 ± 2.9	153 ± 15
o-Xylene[b]	1.00	128 ± 4.2	160 ± 10
Methyl sulfoxide	1.00	116 ± 0.7	119 ± 11
Propyl benzene[b]	0.99	132 ± 4.3	160 ± 13
1,3,5-Trimethylbenzene[b]	0.99	136 ± 2.8	166 ± 11
2-(2-Methoxyethoxy)ethanol	1.00	124 ± 0	128 ± 8.0
1,2,4-Trimethylbenzene	0.99	133 ± 1.4	160 ± 8.5
1,2,3-Trimethylbenzene[b]	0.99	130 ± 0.78	156 ± 4.0
Diethylene glycol	1.00	112 ± 3.5	96 ± 6.5
Dipropylene glycol	0.97	117 ± 3.6	106 ± 7.0
2-(2-Butoxyethoxy)ethanol	1.00	163 ± 3.6	143 ± 13
2-(2-Butoxyethoxy)ethyl acetate	1.01	128 ± 0.7	123 ± 10
Texanol	1.10	150 ± 2.6	146 ± 10

[a] Spike level below the method quantifiable limit.

polar compound. Precision was good (RSD values <10%). Recovery of the aromatic targets (i.e., xylenes and trimethyl benzenes) were very high for controls prepared and analyzed for the storage stability study. Although these recoveries were high, these compounds were not measured at detectable levels during bulk product analysis.

7.3.3 Storage Stability

In order to evaluate the stability of the paint samples over prolonged storage periods, bulk product analysis of paint samples was performed at the time the first small chamber emissions tests were performed (T=7 weeks after aliquoting) and at the time the last small chamber emissions tests were performed (T=29 weeks after aliquoting). As discussed in Section 5 paint samples were stored in screw cap glass vials at room temperature in the dark.

A review of the results for the latex paints indicated the external quantitation standard was compromised in the highest calibration standards used for the bulk product analyses for both time periods. If these high standards were removed from the calibration curve, many of the target VOCs exceeded the upper calibration limit. As a result, all alkyd sample extracts prepared for the bulk product analyses were diluted and reanalyzed. For the alkyd paints, the results from the reanalyzed extracts are presented in this report. Results of the analyses are given for the alkyd paints in Table 7-12 and the latex paint in Table 7-13. The results for method controls associated with these paint samples are given in Tables 7-10 and 7-11. In each table, measured concentrations for target analytes and TVOC are given for each time period. The ratio of measured concentrations for paint samples stored for 29 weeks and 7 weeks of storage is also given. If there were no sample losses during storage, the ratio for these two measured concentrations should be 1.0. Ratios less than 1.0 indicate losses during storage. Results for the alkyd paints show a uniform ratio of ~0.70 suggesting approximately 30% loss of volatile constituents during storage. Although this is likely, the magnitude of the losses are similar to those seen for method controls prepared and analyzed at the same time (Table 7-10). Consequently, there could have been a uniform analytical bias during the analyses of the paint samples after storage. Unfortunately, it was not possible to determine if this was the case or if decreases in measured paint concentrations over time were due to volatility losses during storage. These are the same trends that were seen for the analyses performed at the time the samples were prepared.

For the latex paint samples, the ratio of measured analyte concentrations at 29 and 7 weeks of storage ranged from 0.50 to 1.30. Lowest ratios are seen for the most polar

TABLE 7-12. RESULTS OF THE STORAGE STABILITY TESTS FOR ALKYD PAINTS

Compounds	Glidden/Gloss (Hyacinth) T=7 Weeks (mg/g)	Glidden/Gloss (Hyacinth) T=29 Weeks (mg/g)	Ratio[a]	Sherwin Williams/Semi-gloss (Violet Veil) T=7 Weeks (mg/g)	Sherwin Williams/Semi-gloss (Violet Veil) T=29 Weeks (mg/g)	Ratio
m,p-Xylene	3.58	2.66	0.74	5.14	3.64	0.71
n-Nonane	9.82	7.66	0.78	9.76	6.54	0.67
o-Xylene	1.06	0.817	0.77	0.781	0.554	0.71
Propylcyclohexane	4.19	3.03	0.72	3.24	2.23	0.69
3- & 4-Ethyl toluene	1.82	1.38	0.76	0.694	ND[b]	–
1,3,5-Trimethylbenzene	0.788	0.623	0.79	0.322	0.209	0.65
n-Decane	18.0	14.0	0.78	15.9	11.4	0.72
2-Ethyl toluene	0.617	0.474	0.77	ND	ND	–
1,2,4-Trimethylbenzene	2.76	2.08	0.75	0.854	0.608	0.71
1,2,3-Trimethylbenzene	0.839	0.640	0.76	ND	ND	–
2-Methyldecane	1.98	1.48	0.75	2.49	1.68	0.68
trans-Decahydronaphthalene	2.10	1.56	0.74	2.58	1.85	0.72
n-Undecane	9.11	6.96	0.76	14.0	10.4	0.74
Pentylcyclohexane	0.518	0.483	0.93	1.54	1.17	0.76
n-Dodecane	2.60	1.96	0.75	6.90	4.65	0.67
TVOC	284	274	0.96	314	276	0.88

[a] Ratio of measured concentrations at T=29 weeks to T=7 weeks.

[b] Below the method quantitation limit.

TABLE 7-13. RESULTS OF THE STORAGE STABILITY TESTS FOR LATEX PAINTS

	Glidden Semigloss (Down Yonder)			Sherwin Williams Flat (Marmalade)		
Compounds	T=7 Weeks (mg/g)	T=29 Weeks (mg/g)	Ratio[a]	T=7 Weeks (mg/g)	T=29 Weeks (mg/g)	Ratio
2-Methyl-2-propanol	ND[b]	ND	NC[c]	ND	ND	NC
Ethylene glycol	19.1	14.3	0.75	29.0	26.8	0.92
1,2-Propanediol	38.3	31.0	0.81	ND	ND	NC
m,p-Xylene	ND	ND	NC	ND	ND	NC
n-Butyl ether	ND	ND	NC	ND	ND	NC
o-Xylene	ND	ND	NC	ND	ND	NC
Methyl sulfoxide	ND	ND	NC	ND	ND	NC
Propyl benzene	ND	ND	NC	ND	ND	NC
1,3,5-Trimethylbenzene	ND	ND	NC	ND	ND	NC
2-(2-Methoxyethoxy)ethanol	ND	ND	NC	ND	ND	NC
1,2,4-Trimethylbenzene	ND	ND	NC	ND	ND	NC
1,2,3-Trimethylbenzene	ND	ND	NC	ND	ND	NC
Diethylene glycol	ND	ND	NC	5.14	3.44	0.67
Dipropylene glycol	1.23	0.946	0.77	0.347	0.285	0.82
2-(2-Butoxyethoxy)ethanol	4.42	4.94	1.11	1.54	1.42	0.90
2-(2-Butoxyethoxy)ethyl acetate	0.498	0.247	0.50	ND	ND	NC
Texanol	5.72	7.39	1.30	5.13	5.76	1.12
TVOC	69.3	58.8	0.85	41.2	37.7	0.92

[a]Ratio of measured concentration at T=29 weeks to T=7 weeks.
[b]Below the method quantifiable limit.
[c]Not calculated.

compounds (diethylene glycol, dipropylene glycol, and ethylene glycol) or compounds that have relatively low concentrations (2-(2-butoxyethoxy)ethyl acetate). These compounds would be expected to give the poorest analytical performance. Thus although there appear to be some losses during storage, a low ratio could also reflect analytical performance.

SECTION 8.0
SMALL CHAMBER EMISSIONS TESTS

8.1 OVERVIEW AND STUDY DESIGN

Small chamber tests are intended to measure emissions from paint samples over time for individual VOCs/SVOCs and TVOC using carefully controlled conditions. During testing, a paint sample is applied to a glass plate which is immediately placed in a 52.7 L stainless steel chamber. The chamber is sealed and air is passed through the chamber at a rate of one air change per hour (ACH). Air samples are collected from the chamber outlet at specified time points for measuring VOC/SVOC and aldehyde emissions.

During the previous work, VOCs/SVOCs in chamber air samples were collected on Tenax GC cartridges with subsequent thermal desorption and GC/MS analysis (1). Unfortunately, problems were encountered when applying this method to emissions testing for both alkyd and latex paints. For alkyd paints, high concentrations of VOCs in air samples from the small chambers caused several problems. For example,

- The mass of VOCs analyzed from the sorbent cartridges exceeded the linear dynamic range of GC/MS analysis, unless very small sample volumes were collected.
- The collection of small sample volumes resulted in poor precision.
- The preparation of vapor phase standards at very high VOC concentrations was difficult.

For the latex paints, the polar SVOCs such as Texanol and 2-(2-butoxyethoxy)ethanol were not recovered from large Tenax GC cartridges during thermal desorption.

To overcome these problems, a first step on this work assignment was to modify and evaluate sampling and analysis methods for measuring VOC/SVOC emissions from paint samples. Activated charcoal-based sampling tubes with solvent extraction and GC/MS analysis of sample extracts was evaluated for estimating VOC emissions from alkyd paint samples. The charcoal method was considered advantageous in that large sample volumes (e.g., 5 to 20 L) can be collected even when the concentrations of the VOCs are high. Solvent extracts can then be diluted as required to obtain analyte concentrations within the linear range of the GC/MS system. Sample collection on small Tenax TA sample cartridges followed by thermal desorption and analysis by GC/MS or gas chromatography/flame ionization detection (GC/FID) was proposed for measuring SVOC emissions from latex paint samples. This method has been reported previously for the sampling and analysis of polar SVOCs, although performance results had not been reported (6 and Appendix A). It was felt that more efficient desorption of SVOCs might be achieved compared to the Tenax GC method used previously, since higher desorption temperatures and smaller diameter tubes are used. For both of the proposed sampling and analysis methods, recovery tests were performed to determine the precision and accuracy of the method. Tests were also performed to determine the dynamic range of the methods.

After acceptable performance was demonstrated for the proposed sampling and analysis methods, a series of small chamber tests were performed to evaluate overall method performance for the determination of VOC/SVOC and aldehyde emissions from latex and alkyd paints. Table 8-1 outlines the tests that were performed. As shown in the table, Tests 1 and 2 were range finding tests for the latex and alkyd paints. These range finding tests were performed to determine the appropriate air sample collection volumes, sample collection time points, and test durations for the two type of paints. Tests 3 to 6 were single chamber repeatability tests designed to determine method precision for the same test chamber for both an alkyd and a latex paint. Once acceptable precision was demonstrated, Tests 7 to 10 were performed to determine the recovery of target VOCs/SVOCs from the chambers. Single chamber repeatability and interchamber variability tests were then performed (Tests 11 to 18). These eight additional chamber tests were performed to obtain data on the performance of the method for all six types of paints, with the variability being determined for tests performed in the same chamber for three paints and in different chambers for the other three paints. Finally, a set of four chamber tests (Tests 19 to 22) were performed to evaluate the effect of air velocity on emission rates. Results were compared with and without the fan for both an alkyd and a latex paint. VOC/SVOC emissions were measured during all chamber tests. Aldehyde emissions were measured based on preliminary screening tests.

8.2 METHODS

8.2.1 Application of Paint Sample

In order to properly evaluate the small chambers, a reproducible method for applying the wet paint to a glass panel was necessary. In the previous study (1), a brush was used

TABLE 8-1. PERFORMED CHAMBER TESTS FOR QUANTIFICATION OF VOC/SVOC EMISSIONS

Test Number	Description of Test	Paint Type	Gloss Type	Test Duration[a] (Days)	Sampling Time[a] Points (Hrs.)
1	Range finding	Latex (vinyl)	Flat (Marmalade)	5	8,24,72,96,120
2	Range finding	Alkyd	Gloss (Hyacinth)	3	4,8,12,24,72
3	Single chamber repeatability	Latex (vinyl)	Flat (Marmalade)	7	1,12,24,48,96,120,168
4	Single chamber repeatability-Duplicate	Latex (vinyl)	Flat (Marmalade)	7	1,12,24,48,96,120,168
5	Single chamber repeatability	Alkyd	Gloss (Hyacinth)	1	0.5,1,2,3,4,8,12,24
6	Single chamber repeatability-Duplicate	Alkyd	Gloss (Hyacinth)	1	0.5,1,2,3,4,8,12,24
7	Analyte Recovery Tests	VOCs[b]	NA[c]	2	0,1,2,4,8,12,24
8	Analyte Recovery Tests-Duplicate	VOCs	NA	2	0,1,2,3,4
9	Analyte Recovery Tests	SVOCs[d]	NA	2	0,1,-2,-3,4,6
10	Analyte Recovery Tests-Duplicate	SVOCs	NA	2	0,1,2,3,4,6
11	Inter-chamber variability	Alkyd	Flat (Chim Cham)	1	0.5,1,2,3,4,8,12,24
12	Inter-chamber variability-Duplicate	Alkyd	Flat (Chim Cham)	1	0.5,1,2,3,4,8,12,24
13	Inter-chamber variability	Alkyd	Semigloss (Sea Foam)	1	0.5,1,2,3,4,8,12,24
14	Inter-chamber variability-Duplicate	Alkyd	Semigloss (Sea Foam)	1	0.5,1,2,3,4,8,12,24
15	Inter-chamber variability	Latex	Gloss (Rose Dawn)	7	1,12,24,48,96,120,168
16	Inter-chamber variability-Duplicate	Latex	Gloss (Rose Dawn)	7	1,12,24,48,96,120,168
17	Single chamber repeatability	Latex (vinyl)	Semigloss (Down Yonder)	7	1,12,24,48,96,120,168
18	Single chamber repeatability-Duplicate	Latex	Semigloss (Down Yonder)	7	1,12,24,48,96,120,168
19	Effect of air velocity (w/fan)	Latex	Flat (Marmalade)	7	1,12,24,48,96,120,168
20	Effect of air velocity (w/o fan)	Latex	Flat (Marmalade)	7	1,12,24,48,96,120,168
21	Effect of air velocity (w/fan)	Alkyd	Gloss (Bumbershoot)	1	0.5,1,2,3,4,8,12,24
22	Effect of air velocity (w/o fan)	Alkyd	Gloss (Bumbershoot	1	0.5,1,2,3,4,8,12,24

[a] Test duration and sampling times determined in range-finding tests.
[b] Alkyd paint target analytes.
[c] Not applicable.
[d] Latex paint target analytes and aldehydes.

but was considered unacceptable since it did not apply a uniform thickness and consistent amount of paint.

For this study a "drawdown" method utilizing an 11 inch adjustable Microm Film Applicator (Paul M. Gardner Co., Pompano Beach, FL) was used. A standard pane of window glass (12 in. x 14 in.) that had been cleaned, dried and weighed served as the substrate for application. A flat surface with a straight edge secured on one side served as a guide for the applicator and a support for the test glass panel. It is important that this support/surface be as rigid and flat as possible since differences of only several thousandths of an inch caused problems with uniform coatings of the paint samples. The glass plate was secured to the support surface with masking tape to prevent movement during coating. The tape was placed as single pieces stretching across the top and bottom ends of the glass plate. The tape was carefully removed where the runners of the applicator contacted the glass plate. In addition to securing the glass plate to the support surface, the tape served as a resist to the paint. The combination of the tape and the width of the applicator provided an area on the glass 279 x 283 mm for coating with paint. This area allowed a loading of 1.5 m^2/m^3 (paint area to chamber volume).

During application, the paint vials were weighed, then vigorously shaken both manually and with a vortex mixer for approximately 2 minutes before opening. The applicator gate opening was adjusted to 7 mil and placed at the top of the prepared glass pane. A pool of paint was poured onto the top strip of masking tape between the sides of the applicator. With a steady motion, the applicator was pulled through the paint using the straight edge as a guide. When the applicator and excess paint had cleared the glass and were on the bottom strip of tape, the applicator was removed and the strips of masking tape carefully removed. The coated glass was then weighed to determine the wet paint mass. The approximate thickness of the wet paint was 4 mil.

8.2.2 Test Chambers

The small chamber test system used on this work assignment consisted of two electropolished stainless steel chambers housed in a temperature controlled incubator. The chambers have a volume of 52.7 L and are of an identical design to those used at the Air and Energy Engineering Laboratory at the U.S. EPA facility in Research Triangle Park, NC. Nominal dimensions of the chambers are 51 cm (width) by 25 cm (height) by 41 cm (depth). A stainless steel plate, fitted with an O-ring, is used to seal the one open side. The chambers are fitted with inlet and outlet manifolds designed to ensure adequate mixing in the chamber. Air supplied to the chamber is first passed through a series of filtration devices to minimize background contamination. Air flow rates are controlled by mass flow controllers/meters. A water vapor generator is used to control the relative humidity of the air stream. A diagram of this system is given in Figure 8-1. Performance of the chambers has been previously validated [8]. Operating conditions for tests conducted during this work assignment were:

- 23 ± 1°C temperature,
- 50 ± 5% relative humidity (input air),
- 1.0 ± 0.05 air exchange per hour,

Airflow rates, temperature, and relative humidity were monitored continuously during each test; average hourly values were recorded.

During tests 19 to 22 (Table 8-1) small chamber tests were performed with both alkyd and latex paints to determine the effect of air velocity on emission rates. A small fan was installed in one of the small chambers for comparison against another small chamber without a fan. The fan size and configuration was based on the design currently being used by Dr. Bruce Tichenor, Air and Energy Engineering Research Laboratory (AEERL), USEPA, Research Triangle Park, NC. A 1 9/16 inch diameter 12 VDC brushless micro fan (Model No. 273-244A, 3.5 cfm airflow, Radio Shack Division of Tandy Corp., Fort Worth, TX 76102), was suspended by springs between the inlet and exhaust manifolds inside the chamber. The springs were simply hooked in the holes on both ends of the manifold pipes and the mounting holes in the fan. This placed the fan approximately in the center of the chamber 5 inches above the paint sample. The fan was oriented such that the airflow was in the direction of the top of the chamber. Power to the fan was supplied by a variable DC power supply. Power leads to the fan passed through a Teflon faced silicone septum in an unused chamber port. Based on multi-point air velocity measurements inside the chamber using a constant temperature anemometer (CTA), an operating voltage of 9.00 VDC was determined to provide a suitable fan speed. This generated air velocities across the sample plate ranging from 5.9 to 16.2 cm/s depending on the point of measurement. The highest velocities were observed in a diagonal line from the left rear to the right front of the test chamber. The average velocity of the test points was 11.2 cm/s. The velocities measured in the chamber

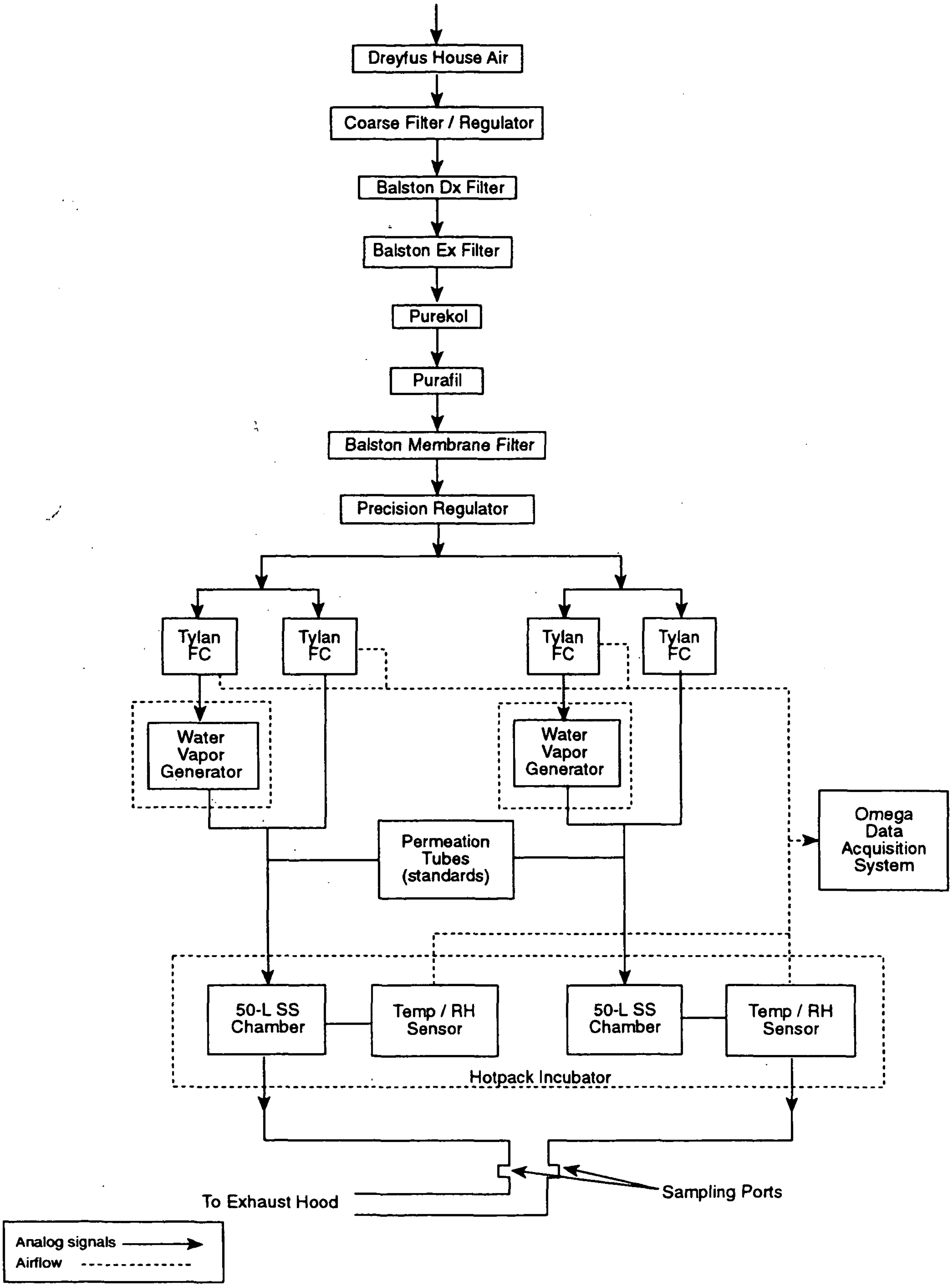

Figure 8-1. Diagram of the Chamber Emissions Test System.

without the fan were below the detection limit of 2 cm/s. A complete description of the air velocity measurements can be found in the report prepared by Peters and Rodes [9].

8.2.3 Sampling and Analysis Methods

8.2.3.1 VOCs from Alkyd Paints

For chamber tests with alkyd paints, VOCs in air samples were collected by passing air from the chamber outlet through sampling tubes (7 cm x 6 mm o.d.) containing two sections of activated coconut shell charcoal (charcoal tubes, No. 226-01GWS, SKC, Inc., Eighty-four, PA). Sample flow rates ranged from approximately 200 to 265 mL/min. Sampling times varied from 10 to 75 minutes to give nominal sample volumes ranging from 2 to 20 L.

VOCs were extracted from the sorbent material by combining then extracting both portions of the sample tube charcoal beds with 2 mL of carbon disulfide. Samples were spiked with the external quantitation standard, o-xylene-d_{10}, during extraction. Aliquots (1 µL) of the sample extracts were immediately analyzed by GC/MS using the conditions given in Table 7-1. Instrument calibration and quantitation of VOCs in sample extracts was performed using relative response factor (RRFs) as described in Section 7.2.2. Calibration standards of target analytes in carbon disulfide were prepared at six levels ranging in concentration from 0.5 ng/µL to 500 ng/µL for each of the target VOCs.

Concentrations of target VOCs in sample extracts (C_{EX}) were converted to chamber air concentrations (C_{CA}) as

$$C_{CA}(ng/L \ or \ \mu g/m^3) = \frac{C_{EX}(ng/\mu L) \cdot V_{EX}(\mu L)}{V_{CA}(L)} \tag{8-1}$$

where V_{EX} is the volume of the extract and V_{CA} is the volume of the collected air sample.

8.2.3.2 SVOCs from Latex Paints

For chamber tests with latex paints, SVOCs in air samples were collected by passing air from the chamber outlet through Tenax TA cartridges (200 mm x 6 mm o.d., Envirochem, Kimblesville, PA). Sample flow rates ranged from approximately 30 to 45 mL/min. Sampling times varied from 20 to 80 minutes to give nominal sample volumes ranging from 0.5 to 5 L.

Exposed cartridges were analyzed by thermal desorption followed by GC/MS or GC/FID using the conditions shown in Table 8-2 and 8-3.

TABLE 8-2. GC/MS OPERATING CONDITIONS FOR ANALYSIS OF SVOC EMISSIONS FROM LATEX PAINT SAMPLES

Parameter	Setting
THERMAL DESORPTION	
Thermal desorption temperature	275°C (max 320°C)
Valve and fitting temperature	220°C
Cryo trap temperature	
- minimum	-190°C
- maximum	255°C
Purge Flow Rate	69 mL/min
GAS CHROMATOGRAPH	
Instrument	Hewlett-Packard 5890
Column	DB624-30M widebore fused silica capillary column
Temperature Program	35°C(5 min) to 250°C(2 min) at 5°C/min
Carrier gas flow rate	2.3 mL/min
MASS SPECTROMETER	
Instrument	Hewlett Packard, Model 5988A
Ionization Mode	Electron Ionization Scan 25-350 m/z
Emission Current	0.3 mA
Source Temperature	200°C
Electron Multiplier	2000 volts[a]

[a]Typical value

TABLE 8-3. GC/FID OPERATING CONDITIONS FOR ANALYSIS OF SVOC EMISSIONS FROM LATEX PAINT SAMPLES

Parameter	Setting
THERMAL DESORPTION	
Thermal desorption temperature	275°C
Valve and fitting temperature	220°C
Cryo trap temperature	
-minimum	-200°C
-maximum	255°C
Air flow rate	300 mL/min
Hydrogen flow rate	50 mL/min
Makeup flow rate	30 mL/min
Purge flow rate	30 mL/min
GAS CHROMATOGRAPH	
Instrument	Varian 3700
Column	DBWAX - 30 m x 0.32 mm
Temperature Program	35°C (5 min) to 185°C at 5°C/min
Carrier gas flow rate	2 mL/min
Detector	Flame ionization

During GC/MS analysis, identification of target analytes was based on chromatographic retention times relative to standards and the relative abundances of extracted ion fragments selected for quantitation. Quantitation was accomplished using chromatographic peak areas derived from extracted ion profiles. Calibration standards containing the target analytes were prepared on Tenax TA cartridges at masses ranging from 20 to 5000 ng/cartridge. Each calibration standard and sample contained a known mass of the quantitation standard, bromopentafluorobenzene.

Relative response factors (RRF) were calculated as

$$RRF_T = \frac{A_T \cdot M_{QS}}{A_{QS} \cdot M_T} \qquad (8\text{-}2)$$

where M_T is the mass of target analyte (ng/cartridge), M_{QS} is the mass of quantitation standard (ng/cartridge), A_T is the peak area of the target analyte, and M_{QS} is the mass of the quantitation standard (ng/cartridge).

Because the instrumental response was not linear over the entire calibration range for many of the SVOC targets, the standards used for quantitation were determined by the amount of target analyte found on the samples. In most cases, the analyte amount in the samples was greater than the highest amount in the calibration standard. Where this occurred, the RRF from the highest standard was used for quantitation. This approach was considered acceptable, since GC/MS analysis was only performed during range finding tests. During each day of analysis, an additional standard was analyzed. If the RRF values for this standard were within ±25% of the RRFs obtained for the same concentration standard during the instrument calibration, the GC/MS system was considered "in control" and the appropriate RRF values from the calibration standards were used to calculate the mass of the target SVOCs on sample cartridges (M_T) as

$$M_T = \frac{A_T \cdot M_{QS}}{A_{QS} \cdot RRF_T} \qquad (8\text{-}3)$$

For GC/FID analysis, identification of target analytes was based on chromatographic retention times relative to standards. Quantitation was accomplished using response factors (RFs) generated from chromatographic peak areas. Calibration standards containing target analytes were prepared on Tenax TA. Response factors for each standard were calculated as

$$RF_T = \frac{A_T}{M_T} \tag{8-4}$$

where M_T is the mass of target analyte (µg/cartridge) and A_T is peak area of target analyte.

Mean values and standard deviations of the RFs were calculated for each target SVOC. The calibration curve was considered acceptable if the standard deviation for each response factor was less than 30%. During each day of analysis, an additional standard was analyzed. If the RF values for this standard were within ±25% of the RFs obtained for the same concentration standard during calibration, the GC/FID system was considered "in control". The mean RF values generated during calibration were used to calculate the amount of the target SVOCs on the sample cartridge as

$$M_T(\mu g/cartridge) = \frac{A_T}{R_T} \tag{8-5}$$

For all analyses, chamber air concentrations were calculated by dividing M_T by the sample volume in liters. Since the target analytes were the only compounds in the air samples, TVOC concentrations were calculated by summing individual analyte concentrations.

8.2.3.3 Aldehydes

During chamber tests, aldehydes in air samples were collected by passing air from the chamber outlet through silica gel cartridges impregnated with 2,4-dinitrophenylhydrazine (DNPH) (Waters Assoc., Medford, Ma). Sample flow rates were approximately 400 mL/minute. Sampling times varied from 25 to 75 minutes to give nominal sample volumes of 10, 20, and 30 L.

DNPH/aldehyde derivatives on the sample cartridges were extracted by eluting each cartridge with 5 mL of HPLC grade acetonitrile into a 5 mL volumetric flasks. The final volume was adjusted to 5.0 mL and the samples aliquoted for analysis. Blank cartridges were eluted with each sample set to identify background contaminants. Additional blank cartridges were spiked with known amounts of DNPH/aldehyde standards as a means of assessing recovery.

DNPH/aldehyde derivatives in sample extracts were analyzed by HPLC with UV detection using the conditions shown in Table 8-4. Purified and certified DNPH derivatives of the target aldehydes were purchased for the preparation of calibration solutions. Target aldehydes were identified by comparison of their chromatographic retention times with those of the purified standards. Quantitation of the target compounds was accomplished by the external standard method using calibration standards prepared in the range 0.02 to 15 ng/µL of the DNPH/aldehyde derivatives. Standards were analyzed singly for the aldehyde DNPH derivatives and a calibration curve (through zero) was calculated by linear regression of the concentration and chromatographic response data. All calibration curves had $r^2 \geq 0.998$.

To demonstrate on-going instrumental performance, a calibration standard was analyzed each day prior to the analysis of any samples. The calibration was considered "in control" if the measured concentration of the aldehyde/DNPH derivatives in the standard were 85 to 115% at the real value.

The concentration of each target analyte in chamber air samples was calculated as:

$$C_x = \frac{C_y \; x \; V_y \; x \; D_F}{V_s} \qquad (8\text{-}6)$$

where C_x = Concentration of aldehyde in the sample (µg/m^3)

C_y = Concentration of DNPH/analyte derivative in the sample extract (ng/µL)

V_y = Total volume of sample extract (i.e., 5000 µL)

V_s = Sample volume in liters

D_F = Molecular weight of analyte ÷ molecular weight of analyte/DNPH derivative

8.3 RESULTS

8.3.1 Performance of Paint Application Methods

The performance of the paint application method was evaluated by comparing the wet and dry masses of the paint applied to duplicate small chamber test plates. A summary of these results are shown in Table 8-5. In addition to the masses, the thickness of the dried paint samples was determined by gently removing 0.5 in. square chips of the dried paint film

TABLE 8-4. HPLC OPERATING CONDITIONS FOR THE ANALYSIS OF ALDEHYDE EMISSIONS FROM PAINT SAMPLES

Parameter	Setting
Instrument	Waters Series 510
Column	NOVA-PAK C18, 3.9 x 150 mm
Solvent System	A: Water/Acetonitrile/Tetrahydrofuran 60/30/10 v/v B: Acetonitrile/Water 40/60/v/v
Gradient	100% A for 3 min; then a linear gradient to 100% B in 10 min. Hold 15 min at 100% B
Mobile Phase Flow Rate	1.5 mL/min
Injection Size	20 µL
UV Wavelength	360 nm

TABLE 8-5. PERFORMANCE OF PAINT APPLICATION METHODS

					Mass Applied (g)		Dry Film Thickness (mils)						
Paint Type	Finish	Mfg.	Test	Paint Color	Wet	Dry	Point 1	Point 2	Point 3	Point 4	Point 5	Mean	% RSD
Latex	Flat	SW[a]	1	Marmalade	11.18	5.67	1.9	1.8	1.8	1.8	2.6	2.0	17.6
		SW	3	Marmalade	12.74	6.18	2.0	1.9	1.9	2.0	1.8	1.9	4.4
		SW	4	Marmalade	11.80	5.75	1.8	1.9	1.8	1.9	1.9	1.9	2.9
		SW	19	Marmalade	9.13	4.46	1.9	1.8	1.4	1.5	1.4	1.6	14.9
		SW	20	Marmalade	10.60	5.13	1.8	1.7	1.6	1.6	1.6	1.7	5.2
				Mean:	11.09	5.44							
				% RSD:	12	12							
	Semigloss	GL[b]	17	Down Yonder	7.12	3.16	1.3	1.1	0.9	1.2	0.9	1.1	16.4
		GL	18	Down Yonder	8.29	3.48	1.4	1.3	1.0	1.3	1.1	1.2	13.1
				Mean:	7.71	3.32							
				% RSD:	11	6.8							
	Gloss	SW	15	Rose Dawn	10.79	5.23	1.7	1.5	1.6	1.7	1.6	1.6	5.2
		SW	16	Rose Dawn	10.48	5.16	1.6	1.5	1.3	1.5	1.5	1.5	7.0
				Mean:	11	5.2							
				% RSD:	2.1	0.95							
Alkyd	Flat	GL	11[c]	Chim Cham	13.53	9.76	2.7	2.4	NM[d]	2.5	1.5	2.3	23.4
		GL	12[c]	Chim Cham	14.83	12.11	2.6	2.6	NM[d]	2.7	2.4	2.6	4.9
				Mean:	14.18	10.94							
				% RSD:	6.5	15							
	Semigloss	GL	13	Seafoam	11.19	7.97	2.3	2.2	2.0	2.2	2.0	2.1	5.4
			14	Seafoam	12.23	8.54	2.3	2.5	2.1	2.3	2.5	2.3	6.1
				Mean:	11.71	8.26							
				% RSD:	6.3	4.9							
	Gloss	GL	2	Hyacinth	9.72	6.39	2.0	1.4	1.4	2.0	2.5	1.9	25.1
			5	Hyacinth	9.50	6.39	1.5	1.9	1.8	1.8	3.0	2.0	28.9
			6	Hyacinth	8.78	5.88	1.8	1.8	1.5	2.0	2.9	2.0	26.7
				Mean:	9.33	6.22							
				% RSD:	5.3	4.7							
		SW	21	Bumbershoot	7.09	4.08	1.6	1.3	1.5	1.4	1.1	1.4	13.9
			22	Bumbershoot	7.56	4.31	1.7	1.7	1.2	1.7	1.5	1.6	14.0
				Mean:	7.33	4.20							
				% RSD:	4.5	3.9							

[a]SW - Sherwin Williams
[b]GL - Glidden
[c]Paint could not be removed as a chip for measurement. Thickness determined using a micrometer.
[d]Not measured, micrometer could not reach middle test point.

from five representative locations on each test plate. The thickness of these chips was then measured with a dial indicator.

8.3.2 Performance of Test Methods

8.3.2.1 VOC Emissions from Alkyd Paints

Sampling and Analysis Methods

Evaluations of the sampling and analysis methods for measuring VOCs from alkyd paint samples were performed to determine the accuracy, precision, background contamination, and linear dynamic range of the proposed method for quantitating VOCs in chamber air.

Accuracy was evaluated as % recovery for target VOCs spiked directly onto the sampling cartridge. Preliminary experiments were performed to demonstrate that target VOCs could be recovered from the charcoal sampling tubes. Since it became important to decrease method detection limits, it was also important to demonstrate that low levels of targets were recovered well from the charcoal tubes. During testing, target chemicals were spiked directly onto the tubes at several different levels (2 to 100 ug/sample). Tubes were extracted and extracts analyzed by GC/MS using procedures described for sample analysis above. Percent recovery was calculated as

$$\%\ Recovery = \frac{Amount\ Measured\ x\ 100\%}{Amount\ Spiked} \tag{8-7}$$

Results for these recovery tests are given in Table 8-6. Percent recoveries at all spiking levels were considered acceptable and ranged from 104 to 133%. For the preliminary tests, recoveries were also relatively uniform across spiking levels.

Method controls were prepared and analyzed throughout the chamber emissions testing. Spiking levels and % recovery values for these controls are also given in Table 8-6. Mean recoveries ranged from 104 to 113% for these controls indicating acceptable performance.

Method precision was evaluated as the % RSD of replicate recovery measurements. Data for this parameter are also given in Table 8-6 for both the preliminary recovery tests and the method controls. Results show excellent method precision for replicate samples with RSD values ranging from 0 to 13%.

TABLE 8-6. ANALYSIS OF VOC EMISSIONS FROM ALKYD PAINT - % RECOVERY FROM METHOD CONTROLS (MC)

	MC-High (n=3)[a]			MC-Medium (n=3)[a]			MC-Low (n=3)[a]			MC Test (n=6)[b]		
Compound	Spike Level (µg/sample)	% Recovery	%RSD	Spike Level (µg/sample)	% Recovery	%RSD	Spike Level (µg/sample)	% Recovery	%RSD	Spike Level (µg/sample)	% Recovery	%RSD
m,p-Xylene	100	123	2	10	119	1	4	118	0	13	107	8
n-Nonane	45	128	3	5	123	5	2	118	3	6	108	5
o-Xylene	50	114	1	5	112	4	2	110	1	6	104	9
Propylcyclohexane	50	127	4	5	131	6	2	124	1	6	110	5
3- & 4-Ethyl toluene	99	123	3	10	120	4	4	117	1	13	117	8
1,3,5-Trimethylbenzene	50	118	3	5	117	1	2	111	1	6	111	8
n-Decane	46	132	2	5	132	9	2	119	4	6	114	8
2-Ethyl toluene	49	118	2	5	117	3	2	113	1	6	106	7
1,2,4-Trimethylbenzene	49	114	0	5	113	3	2	109	1	6	106	12
1,2,3-Trimethylbenzene	49	112	2	5	105	2	2	104	2	6	107	9
2-Methyldecane	46	133	3	5	130	7	2	123	8	6	109	6
trans-Decahydronaphthalene	50	130	4	5	125	4	2	117	6	6	112	10
n-Undecane	46	129	5	5	125	4	2	115	2	6	109	9
Pentylcyclohexane	48	120	1	5	121	4	2	110	2	6	113	7
n-Dodecane	47	133	4	5	122	2	2	104	13	6	112	8

[a]Results of preliminary testing
[b]Results of method controls prepared and analyzed as part of small chamber testing

Unspiked sampling cartridges and air samples collected from blank chambers were extracted and analyzed to assess background contamination. None of the target VOCs were detected above the quantitation limit in any of these blank samples.

The linear dynamic range of the method for quantitating VOCs in chamber air was determined based on the dynamic range of the calibration curve and the range of sample volumes collected during emissions testing. During instrumental calibration, linearity for all VOC target analytes was demonstrated for standards in the range 0.5 to 500 ng/µL. The instrument was considered linear if the RRF values did not change substantially as the concentration changed. An example of the relative response factors generated over the calibration range during instrumental calibration is given in Appendix C. Standard concentrations (C_{std}) were then converted to air concentrations (C_{air}) as

$$C_{air}\ (mg/m^3) = \frac{C_{std}(ng/\mu L)\ x\ 2000\ \mu L}{V_{air}(L)\ x\ 1000} \tag{8-8}$$

where V^{air} is the volume of the chamber air sample collected for analysis. The calculated linear dynamic range using this approach was 0.05 to 2000 mg/m^3 for all target VOCs. During small chamber tests, this range was found acceptable for quantitating emissions over a 24-hour test period.

Chamber Test Method

Chamber recovery tests were performed to demonstrate that the chamber test method could be used to accurately measure VOC emissions from alkyd paint samples. These tests were designed to measure recovery of selected target VOCs in the chamber outlet air in the presence of a constant concentration source. The decay in chamber concentrations over time after the source had been removed from the chamber was also monitored to evaluate sink effects within the chamber. This was considered important for compounds that gave poor recoveries. VOCs were selected for the recovery tests that represented the range of volatilities found in the chamber air samples during emission tests. The concentrations of VOCs selected for study were similar to those measured during the first hour of emissions testing with actual paint samples.

During testing, a constant concentration of VOCs was generated using a syringe pump that injected a small, constant volume of a neat mixture of the target compounds into the gas stream entering the chamber. A Brownlee Labs Micro Gradient SFC system was used to deliver a constant volume (0.1 to 1 μL/minute) of the neat mixture to the heated inlet air. The air was passed though a heated glass mixing bulb and a heated transfer line into the chamber. This vapor mixture was then introduced directly into the chamber for a minimum of 24 hours.

During the first test (chamber A, Test 7 in Table 8-1), samples of the inlet air mixture were collected at three time points during the 24-hour equilibration period. This was done to assure that a constant concentration mixture was generated. For chamber B (Test 8 in Table 8-1), only a single inlet sample was collected at the end of the equilibration period. After the equilibration period (approximately 24 hours), air samples were also collected at the chamber outlet. Once sample collection under constant concentration conditions was complete, the vapor generator was turned off thus removing the source from the chamber. Additional samples were then collected from the chamber outlet at selected time points after the source had been removed. All collected samples were extracted and analyzed for target VOCs as described above. Percent recovery for the target VOCs from the test chamber were then calculated as

$$\%\ Recovery = \frac{C_{in}}{C_{out}}\ x\ 100\% \tag{8-9}$$

where C_{in} was the air concentration measured in the air mixture prior to introduction into the test chamber. C_{out} was the air concentration measured in the chamber outlet air.

Data for the chamber recovery study are provided in Table 8-7 which gives the measured VOC concentrations in the chamber inlet air and the % recovery of the target VOCs in the chamber outlet air. For the samples collected after the source had been removed, the % recovery value that would occur in the absence of sink effects is also given as the theoretical % recovery. Several important observations can be made from the data provided in Table 8-7.

- The low variability in the VOC air concentrations at the chamber inlet suggests that constant concentration conditions were achieved during the chamber equilibration period.
- Good recoveries were calculated for all of the test compounds under constant concentration conditions (T=O) suggesting minimal losses of target VOCs during emissions testing.

TABLE 8-7. CHAMBER RECOVERY TESTS FOR ALKYD PAINT COMPONENTS

Compound	Mean Inlet Concentration ±SD (mg/m^3)	% Recovery T=0[a]	T=1.1	T=2.1	T=3.1	T=4.1	T=8.3	T=12.6	T=24.6
TEST 7 (CHAMBER A)									
m,p-Xylene	100±12	101±2	38	13	NT[b]	2.0	ND[c]	ND	ND
n-Nonane	210±22	104±7	42	18	NT	2.6	0.057	ND	ND
o-Xylene	32±3	107±1	37	13	NT	2.0	ND	ND	ND
Propylcyclohexane	130±18	109±2	41	16	NT	2.4	0.054	ND	ND
n-Decane	280±31	104±4	59	26	NT	4.4	0.12	0.047	0.017
1,2,4-Trimethylbenzene	68±5	96±4	34	13	NT	2.0	ND	ND	ND
trans-Decahydronaphthalene	99±9	105±7	36	15	NT	2.2	0.061	ND	ND
n-Undecane	140±23	108±2	45	18	NT	3.0	0.13	0.068	ND
Pentylcyclohexane	16±2	104±8	34	14	NT	ND	ND	ND	ND
n-Dodecane	43±4	106±3	35	14	NT	2.4	0.18	ND	ND
TEST 8 (CHAMBER B)									
m,p-Xylene	100	100±15	38	16	6.9	2.7	NT	NT	NT
n-Nonane	180	103±18	57	21	8.4	3.5	NT	NT	NT
o-Xylene	33	99±11	43	14	5.7	2.6	NT	NT	NT
Propylcyclohexane	130	93±7	42	16	7.2	3.3	NT	NT	NT
n-Decane	240	114±5	69	28	14	5.7	NT	NT	NT
1,2,4-Trimethylbenzene	58	110±17	43	16	6.5	3.0	NT	NT	NT
trans-Decahydronaphthalene	91	109±10	45	17	8.3	3.1	NT	NT	NT
n-Undecane	120	109±3	48	19	8.2	4.2	NT	NT	NT
Pentylcyclohexane	17	99±17	34	14	6.2	ND	NT	NT	NT
n-Dodecane	40	108±9	43	17	7.7	3.6	NT	NT	NT
THEORETICAL % RECOVERY[d]		100	33.3	12.2	4.5	1.7	0.025	3.3×10^{-4}	0

[a]For test 7, n=3; for test 8, n=2.
[b]Not tested.
[c]Below the method quantitation limit of 0.05 mg/m^3.
[d]Calculated as $C_t = C_o \cdot e^{-rt}$
where r is the air exchange rate (h^{-1}), t is time after source removal, C_t is air concentration at t, and C_o is air concentration before source removal.

- Measured recoveries after the source was removed from the chamber inlet (T=1.1 to 24.6) agreed well with the theoretical recoveries indicating that the test chamber contains few sinks for the target VOCs. Greatest deviations appeared to occur for the n-alkanes whose chamber air concentrations appeared to decay more slowly than predicted in the absence of sink effects.
- Results for the two chamber tests were similar suggesting good reproducibility of the overall small chamber method.

8.3.2.2. SVOC Emissions from Latex Paint Samples

Sampling and Analysis Method

Evaluations of the method for quantitating SVOC emissions in chamber air samples are similar to those described above. Tests were performed to determine the accuracy, precision, background contamination, and linear dynamic range for the sampling and analysis method.

Several of the SVOCs that are emitted from latex paint samples are very polar compounds which present problems during chromatographic analysis. Most importantly, when a small mass is injected into a GC column, adsorptive losses may occur. As a result, a linear calibration curve cannot be generated over a large calibration range and response factors or relative response factors will increase with increasing sample mass. This is illustrated in Table 8-8 which gives the relative response factors (RRFs) for target SVOCs generated during GC/MS analysis. As shown in the table, the relatively nonpolar targets such as o-xylene, Texanol, 2-(2-butoxyethoxy)ethyl acetate, and 2-(2-butoxyethoxy)ethanol have relatively constant RRFs over the entire calibration range (25 to 2500 ng). In contrast, the more polar target chemicals (i.e., ethylene glycol, 1,2-propanediol, 2-(2-methoxyethoxy)ethanol, diethylene glycol, and dipropylene glycol) have very low RRFs for the low injected masses with increasing RRF values as the injected mass increases.

GC/MS analysis was only performed for the range find test (Test 1, Table 8-1). Analysis of all other air samples collected for emissions testing was performed by GC/FID. GC/FID analysis was selected since it gives a linear response for high masses injected (i.e., >1 µg). This was considered important since the SVOC levels measured during the range finding tests were so high. Fortunately, only a few SVOCs are emitted from paint samples, thus the use of chromatographic retention times for compound identification was possible.

TABLE 8-8. RELATIVE RESPONSE FACTORS FOR THE ANALYSIS OF SVOC EMISSIONS FROM LATEX PAINT SAMPLES BY GC/MS

		Relative Response Factor per Spiking Level (ng)								
Compound	Ion	25	50	100	250	500	750	1000	1500	2500
Ethylene glycol	62	-	-	-	0.050	0.098	0.11	0.15	0.18	0.18
Ethylene glycol	43	-	-	-	0.014	0.030	0.037	0.050	0.056	0.056
Ethylene glycol	31	-	-	-	0.017	0.029	0.039	0.050	0.055	0.057
1,2-Propanediol	61	-	-	-	0.071	0.11	0.15	0.23	0.26	0.25
1,2-Propanediol	76	-	-	-	0.012	0.021	0.027	0.040	0.048	0.047
2-(2-Methoxyethoxy)ethanol	89	0.35	0.54	0.37	0.55	0.62	0.66	0.81	0.84	0.78
2-(2-Methoxyethoxy)ethanol	59	0.48	0.85	0.52	0.90	1.2	1.4	1.7	2.1	2.1
Diethylene glycol	75	0.42	0.42	0.29	0.59	1.1	1.3	1.8	2.1	2.3
Diethylene glycol	45	0.17	0.16	0.12	0.20	0.42	0.62	0.88	0.89	1.0
Dipropylene glycol	89	0.48	0.76	0.45	0.82	0.96	1.2	1.5	1.7	1.7
Dipropylene glycol	59	0.17	0.24	0.16	0.27	0.33	0.44	0.59	0.69	0.68
2-(2-Butoxyethoxy)ethanol	132	0.098	0.13	0.10	0.12	0.10	0.087	0.094	0.094	0.097
2-(2-Butoxyethoxy)ethanol	89	0.37	0.45	0.37	0.46	0.49	0.48	0.55	0.54	0.52
2-(2-Butoxyethoxy)ethyl acetate	87	2.2	3.5	2.4	3.5	3.8	3.5	3.9	3.8	3.4
2-(2-Butoxyethoxy)ethyl acetate	101	0.32	0.48	0.31	0.44	0.41	0.35	0.40	0.40	0.37
Texanol	173	0.37	0.46	0.38	0.44	0.41	0.33	0.37	0.34	0.32
Texanol	143	0.33	0.40	0.31	0.39	0.36	0.32	0.37	0.33	0.29
o-Xylene	91	4.9	4.5	4.8	4.5	4.4	4.3	4.9	4.8	4.2
o-Xylene	106	2.5	2.4	2.4	2.4	2.1	1.9	2.0	1.8	1.7

The range of the injected mass for calibration was limited during emissions testing and compound amounts were selected for calibration that were in the range expected in the chamber air samples. This was done in order to generate a linear calibration. An example of response factors (RFs) generated by GC/FID for the analysis of chamber air tests is given in Table 8-9. Generally, these response factors do not show a trend of increasing RFs with increasing mass. Exceptions are 1,2-propanediol where the lowest calibration standard shows low RF values compared to the other standards and diethylene glycol where RFs increased with increasing mass over the entire calibration range. In addition to poor linearity over the calibration range, the RFs for diethylene glycol were very erratic. Throughout the sample analysis period, the RF for the daily calibration check was not "in control" (greater than 25% deviation from the mean RF). As a result, quantitative data could not be generated for this compound. This poor performance is probably due to the very polar nature of the compound.

During emissions testing, the linear dynamic range of the test method was estimated based on the air sample volume and the calibration range as described above. The linear dynamic ranges for target SVOCs estimated for the small chamber tests are given in Table 8-10. This range is considerably smaller than that reported for the VOCs from alkyd paints due to the much smaller range for the calibration standards.

Accuracy and precision of the sampling and analysis method were evaluated by determining % recovery and %RSD for target SVOCs spiked onto sampling cartridges. Results of these analyses are given in Table 8-11. As indicated in the table, six method controls were prepared and analyzed throughout emissions testing. Results for one of the controls gave very high % recovery values. It appeared as though this control had been spiked at twice the specified amount. Mean % recovery and %RSD values have been calculated both with and without data from this control. When the high control is deleted, the precision and accuracy of the method appears to be acceptable for all compounds except diethylene glycol. Poor precision for diethylene glycol is consistent with the erratic response found during the daily calibration checks. This result again suggests that quantitative results cannot be generated for diethylene glycol.

Unspiked sampling cartridges and air samples collected from blank chambers were analyzed to assess background contamination. None of the target SVOCs were detected above the quantitation limit in any of the blank samples.

TABLE 8-9. EXAMPLE RESPONSE FACTORS FOR THE ANALYSIS OF LATEX PAINT USING FLAME IONIZATION DETECTION

Compound	Standard Mass (μg)	Response Factor ($X10^4$) X1[a]	X3	X5	X10	X30	X60	Mean	% RSD
1,2-Propanediol	0.186	89.7	118	189	17.7	141	NA[b]	143	29
Ethylene glycol	0.226	161	84.8	142	143	122	132	131	21
2-(2-Butoxyethoxy)ethanol	0.174	184	203	285	263	205	NA	228	19
Texanol	1.2	282	291	402	354	270	NA	319	18
Diethylene glycol	0.067	35.1	45.5	55.8	80.2	89.6	NA	61	38

[a] Mass injected for the standard is equal to the standard mass times the number indicated.
[b] Not analyzed; high standard for ethylene glycol added to allow quantitation of very high concentration air samples.

TABLE 8-10. ESTIMATED LINEAR DYNAMIC RANGE FOR SVOC TEST METHOD

	Air Concentration		
	Lowest Quantifiable[a]		
Compound	mg/m^3	$mg/m^3/g$[b]	Maximum Quantifiable
1,2-Propanediol	0.37	0.037	11
Ethylene glycol	0.53	0.053	32
2-(2-Butoxyethoxy)ethanol	0.35	0.035	10
Texanol	2.4	0.24	72
Diethylene glycol	0.13	0.013	3.9

[a] Defined as method quantitation limit.

[b] Method quantitation limit reported as mg/m^3 per gram of paint; calculated based on a 10 gram paint sample used for chamber testing.

TABLE 8-11. ANALYSIS OF SVOC EMISSIONS FROM LATEX PAINT SAMPLES - METHOD CONTROLS

Compound	Spike Level ($\mu g/m^3$)[a]	% Recovery[b]	%RSD
1,2-Propanediol	1.8	88(107)	4.2(36)
Ethylene glycol	4.6	78(93)	9.4(34)
2-(2-butoxyethoxy)ethanol	1.8	92(109)	21(33)
Texanol	12	94(107)	16(28)
Diethylene glycol	0.68	84(133)	87(86)

[a] Assuming a 0.5 L sample volume.

[b] A total of six method controls were analyzed throughout emissions testing; one control appeared to be spiked at twice the level. Results from this control were deleted from calculations. Values in parentheses were calculated with sixth method control included.

Chamber Test Method

Chamber recovery tests (Tests 9 and 10 on Table 8-1) were performed to demonstrate that the chamber test method could be used to accurately measure SVOC emissions from latex paints. These tests were designed to measure recovery of selected target SVOCs in the presence of a constant concentration source. The decay in chamber air concentrations over time after the source had been removed from the chamber was also measured to evaluate sink effects. The procedures described in Section 8.3.2.1 were used for these tests. Tests were performed in both chambers. SVOCs for testing were selected to represent the most abundant compounds measured during the chamber emission tests. Concentrations generated for testing were selected to be similar to those found during the emissions tests.

Results for the chamber recovery tests are given in Table 8-12. Data are provided on the measured SVOC air concentrations in the chamber air inlet and the % recovery of the target SVOCs in the chamber outlet air. For the samples collected after the source had been removed, the % recovery value that would occur in the absence of sink effects is also given as the Theoretical % recovery. The following observations can be made from the results provided in Table 8-12.

- The low variability in the SVOC air concentrations at the chamber inlet indicate that constant concentration conditions were achieved during the chamber equilibration period.
- Good recoveries were calculated for the test compounds under constant concentration conditions (T=0) suggesting minimal losses of target VOCs during emissions testing.
- Results for the two chamber tests were similar suggesting good reproducibility for the overall small chamber method for measuring SVOC emissions from latex paint samples.
- For all of the test compounds, measured recoveries after the source had been removed (T = 1.2 to 6.2) were higher than the theoretical value in the absence of sink effects. This result suggests that there may be sinks for the SVOCs within the chambers. The trend is most noticeable at the latter time points. Recoveries for 2-(2-butoxyethoxy)ethanol are most similar to the theoretical values suggesting the weakest sink effects. In

TABLE 8-12. CHAMBER RECOVERY TESTS OF LATEX PAINT COMPONENTS

Compound	Mean Inlet Concentration ± SD (mg/m^3)	% Recovery					
		T=0[a]	T=1.2	T=2.2	T=3.2	T=4.2	T=6.2
TEST 9							
1,2-Propanediol	5.3 ± 0.14	94 ± 2	35	14	6.0	2.7	1.1
Ethylene glycol	90 ± 0.57	92 ± 2	38	19	9.4	4.7	1.8
2-(2-Butoxyethoxy)ethanol	3.0 ± 0.07	88 ± 3	27	11	5.6	3.6	1.6
Texanol	18 ± 0.91	100 ± 1	35	15	7.4	4.4	1.9
TEST 10							
1,2-Propanediol	4.2 ± 0.21	131 ± 4	32	15	5.5	5.2	0.19
Ethylene glycol	70 ± 5.6	122 ± 2	38	17	9.1	5.0	1.3
2-(2-Butoxyethoxy)ethanol	3.0 ± 0.71	100 ± 18	23	9.1	4.0	2.1	1.2
Texanol	16 ± 1.2	135 ± 14	32	15	7.5	5.3	1.9
THEORETICAL % RECOVERY[b]		100	30	11	4.0	1.5	0.2

[a]Mean recovery and SD, n=3.
[b]Calculated as $C_t = C_o \cdot e^{-rt}$
where r is the air exchange rate (h^{-1}), T is time (hours) after source removal, C_T is air concentration at T, and C_o is air concentration before source removal.

contrast, recoveries for ethylene glycol show the greatest deviation from the theoretical recovery suggesting the strongest sink effects.

8.3.2.1 Aldehyde Emissions

Aldehyde emissions from paint samples were collected on silica gel/DNPH cartridges. The DNPH/aldehyde derivatives formed during sample collection were eluted with acetonitrile. They were analyzed by HPLC/UV. Because this is a previously validated method (9), performance evaluation studies were not performed; rather quality control samples were analyzed to assess method performance throughout the study. QC samples included method controls, method blanks, and chamber blanks. Method controls were sampling cartridges spiked directly with a solution of aldehyde/DNPH derivatives. Method controls were extracted and analyzed along with chamber air samples. Method blanks were unspiked sampling cartridges that were extracted and analyzed along with chamber air samples. Chamber blanks were 30 L air samples collected from the chamber immediately prior to emissions testing.

Results of these analyses along with information on method quantitation limits are given in Table 8-13. Highest blank and chamber background levels were found for formaldehyde and acetaldehyde. The amounts reported for the method blanks are typical of those found on the DNPH cartridges (9). For these two compounds, the method quantitation limit was determined by the concentration found in the chamber blanks. The recovery data for the method controls indicate acceptable accuracy (% recovery = 80 to 119%) and precision (S.D. = 8.3 to 25%) for all the target aldehydes except acrolein. The reason for poor recovery for this compound is unknown. Since acrolein was not recovered from the method controls, quantitative results are not reported for this compound.

8.3.3 VOC Emissions from Alkyd Paint Samples

Results of the range finding test (Test 2 in Table 8-1) performed with the Glidden gloss alkyd paint (Hyacinth) are given in Table 8-14 and 8-15. Table 8-14 represents measured chamber air concentrates (mg/m^3) for each of the target VOC at each sampling paint. Table 8-15 provides similar data reported as measured air concentration per gram of paint. Results for these tests show a very rapid increase in chamber air content ratios for the target VOCs with a corresponding rapid decay. For most of the target VOCs the highest air concentrations were measured at the first sampling point (t=4.6 hours). Only the least volatile components, n-undecane, pentylcyclohexane and n-dodecane give maximum

TABLE 8-13. METHOD PERFORMANCE DATA FOR ALDEHYDE TESTING

Parameter	Formaldehyde	Acetaldehyde	Acrolein	Propionaldehyde	Benzaldehyde
Amount in method blank ng/sample ± S.D. (n=10)	25 ± 17	59 ± 31	3.0 ±7.9	1.0 ± 3.2	0 ± 0
Concentration in chamber background $\mu g/m^3$ ± S.D.[a] (n=9)	0.85 ± 0.57	2.2 ± 0.40	0.07 ± 0.16	0.02 ± 0.06	0.07 ± 0.17
% Recovery of method controls ± S.D.[a] (n=10)	105 ± 8.3	9 ± 25	NR[e]	89 ± 16	120 ± 17
Method Quantitation Limit					
- Calibration Curve[b]					
ng/sample	43	40	24	25	36
$\mu g/m^3$ (10L)[c]	4.3	4.0	2.4*[f]	2.5*	3.6*
$\mu g/m^3$ (20L)	2.2	2.0	1.2*	1.3*	1.9*
$\mu g/m^3$ (30L)	1.4	1.3	0.80*	0.83*	1.2*
- Chamber blanks[d] - ($\mu g/m^3$)	2.6*	3.4*	0.56	0.26	0.58

[a]Spiked from 71 to 215 ng/sample. Calculated as:

$$\% \ Recovery = \frac{[A]_{MC} - [A]_{MB}}{[A]_S} \times 100\%$$

where $[A]_{MC}$ and $[A]_{MB}$ are the amount measured in the method control and method blank respectively. $[A]_S$ is the amount spiked onto the method control.

[b]Based on the lowest calibration standard analyzed.

[c]Air concentration calculated based on air sample volume in parenthesis.

[d]Equal to the mean plus 3 x S.D. of concentration found in chamber background.

[e]Not recovered.

[f]* indicates method quantitation limit value that was used.

TABLE 8-14. RESULTS OF RANGE FINDING TEST (TEST 2) FOR VOC EMISSIONS FROM ALKYD PAINT[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentrations (mg/m^3)					
TEST 2	T=4.6[b]	T=8.6	T=12.6	T=24.6	T=48.8	T=72.6
m,p-Xylene	29	ND[c]	ND	ND	ND	ND
n-Nonane	160	21	ND	ND	ND	ND
o-Xylene	10	ND	ND	ND	ND	ND
Propylcyclohexane	71	12	ND	ND	ND	ND
3- & 4-Ethyl toluene	33	12	ND	ND	ND	ND
1,3,5-Trimethylbenzene	15	6.9	ND	ND	ND	ND
n-Decane	450	310	110	ND	ND	ND
2-Ethyl toluene	11	ND	ND	ND	ND	ND
1,2,4-Trimethylbenzene	46	25	9.0	ND	ND	ND
1,2,3-Trimethylbenzene	13	8.9	ND	ND	ND	ND
2-Methyldecane	35	33	22	ND	ND	ND
trans-Decahydronaphthalene	39	30	14	ND	ND	ND
n-Undecane	110	150	120	11	ND	ND
Pentylcyclohexane	5.9	8.1	7.3	ND	ND	ND
n-Dodecane	10	17	22	14	ND	ND

[a]Test 2 on Table 8-1, performed using Glidden 4550-76262 Gloss:(Hyacinth); sample wt. - 9.72 g.
[b]Sampling time in hours.
[c]Below the method quantitation limit (5 mg/m^3).

TABLE 8-15. RESULTS OF RANGE FINDING TEST (TEST 2) FOR VOC EMISSIONS FROM ALKYD PAINT[a] - CHAMBER AIR CONCENTRATION PER GRAM OF PAINT

Compound	Chamber Air Concentrations (mg/m^3)					
TEST 2	T=4.6[b]	T=8.6	T=12.6	T=24.6	T=48.8	T=72.6
m,p-Xylene	3.0	ND[c]	ND	ND	ND	ND
n-Nonane	17	2.1	ND	ND	ND	ND
o-Xylene	1.1	ND	ND	ND	ND	ND
Propylcyclohexane	7.3	1.3	ND	ND	ND	ND
3- & 4-Ethyl toluene	3.4	1.2	ND	ND	ND	ND
1,3,5-Trimethylbenzene	1.5	0.72	ND	ND	ND	ND
n-Decane	46	32	12	ND	ND	ND
2-Ethyl toluene	1.1	ND	ND	ND	ND	ND
1,2,4-Trimethylbenzene	4.8	2.6	0.92	ND	ND	ND
1,2,3-Trimethylbenzene	1.3	0.91	ND	ND	ND	ND
2-Methyldecane	3.6	3.4	2.2	ND	ND	ND
trans-Decahydronaphthalene	4.1	3.1	1.5	ND	ND	ND
n-Undecane	11	15	12	1.1	ND	ND
Pentylcyclohexane	0.60	0.83	0.76	ND	ND	ND
n-Dodecane	1.0	1.7	2.3	1.4	ND	ND

[a]Test 2 on Table 8-1, performed using Glidden 4550-76262 Gloss:(Hyacinth); sample wt. - 9.72 g
[b]Sampling time in hours
[c]Below the method quantitation limit

concentrations at later time points. Because of the rapid decay in chamber air concentrations, VOC emissions could not be quantitated at the later time points. Based on the results of this test, sampling points were selected as 0.5, 1, 2, 3, 4, 8, 12, and 24 hours to allow better characterization during the period of highest emissions. In order to reduce the method quantitation limit for sampling of the later time points, larger sample volumes (20 L) were collected and lower concentration standards (0.5 ng/µL) were added for instrument calibration.

Once test conditions were defined, a set of single chamber repeatabilty tests were performed to evaluate the variability of the small chamber emission test for alkyd paint samples when identical conditions (including test chamber and paint type) were used. These two tests, Tests 5 and 6, are described in Table 8-1 and were performed using a Glidden gloss alkyd paint (Hyacinth). Results for the single chamber repeatability tests are given in Tables 8-16 and 8-17. Similar to the range finding tests, results are given for both chamber air concentrations (Table 8-16) and chamber air concentrations per gram of paint (Table 8-17). Each table gives concentration results for both tests at each time point. The variability of the measured concentrations between tests is presented as the %RSD between concentration values for samples collected at the same time point for each test. Results show highest air concentrations for the n-alkanes (n-decane, n-nonane, and n-undecane). For the more volatile compounds, the highest chamber air concentrations are seen for the earliest sample collection points. For example, the highest chamber air concentrations for m,p-xylene are seen at 1.2 hours. In contrast, the highest chamber air concentrations for the less volatile compounds are seen at later time points. For n-undecane, highest air concentrations are seen at 4.1 hours. For n-dodecane, highest air concentrations are seen at 12 hours. These trends are seen for both chamber air concentrations and chamber air concentrations per gram of paint.

Variability between the two tests has been evaluated as the %RSD between paired chamber air concentrations for the two tests. Data in Tables 8-16 and 8-17 show reasonably low %RSD values between the two tests. Slightly better agreement (lower %RSD values) is found when chamber air concentrations are expressed per gram of paint (Table 8-17). For these single chamber repeatability tests, the highest %RSD values were calculated for the most volatile components at the earliest time points. This result may be due to the fact that the samples were placed into the chamber at different times (2 vs. 6 minutes) after the paint application. It is feasible that under these conditions, a substantial and varying fraction of

TABLE 8-16. RESULTS OF SINGLE CHAMBER REPEATABILITY TESTS (TESTS 5 AND 6) FOR VOC EMISSIONS FROM ALKYD PAINTS[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentrations (mg/m^3)							
TEST 5	T=0.65[b]	T=1.2	T=2.1	T=3.1	T=4.1	T=7.8	T=11.8	T=24.8
m,p-Xylene	120	130	92	69	40	4.5	0.45	ND[c]
n-Nonane	250	300	280	250	180	16	3.3	ND
o-Xylene	38	45	32	25	16	2.6	0.30	ND
Propylcyclohexane	89	100	100	110	71	6.7	2.2	ND
3- & 4-Ethyl toluene	48	65	59	58	44	13	4.2	ND
1,3,5-Trimethylbenzene	16	22	22	21	18	6.0	2.7	ND
n-Decane	380	510	570	600	540	140	89	0.58
2-Ethyl toluene	15	19	18	18	15	1.5	1.5	ND
1,2,4-Trimethylbenzene	51	70	68	70	58	19	10	0.19
1,2,3-Trimethylbenzene	14	20	20	21	18	9.0	5.0	0.24
2-Methyldecane	20	30	35	42	41	17	13	0.87
trans-Decahydronaphthalene	33	52	54	57	52	20	13	0.34
n-Undecane	59	100	110	140	140	78	74	15
Pentylcyclohexane	3.6	7.8	8.8	10	10	11	9.9	1.6
n-Dodecane	5.1	9.0	12	13	16	17	19	16
TVOC	5600	7760	7300	7260	5940	1950	1320	176
TEST 6	T=0.70	T=1.2	T=2.2	T=3.2	T=4.2	T=7.9	T=11.9	T=24.9
m,p-Xylene	78	77	54	72	35	3.5	0.34	ND
n-Nonane	190	210	220	250	190	15	3.0	ND
o-Xylene	26	25	20	26	14	2.1	0.25	ND
Propylcyclohexane	78	69	80	84	81	5.2	1.9	ND
3- & 4-Ethyl toluene	39	41	47	49	44	13	4.0	ND
1,3,5-Trimethylbenzene	14	14	18	18	18	6.0	2.4	ND
n-Decane	330	360	530	480	550	150	95	0.48
2-Ethyl toluene	12	12	14	15	14	2.2	1.6	ND
1,2,4-Trimethylbenzene	42	43	58	56	57	20	11	0.21
1,2,3-Trimethylbenzene	11	12	17	16	17	9.0	5	0.23
2-Methyldecane	17	20	32	27	40	14	14	0.73
trans-Decahydronaphthalene	31	32	46	43	55	18	14	0.29
n-Undecane	53	60	110	92	130	82	82	13
Pentylcyclohexane	3.4	3.8	7.1	5.8	9.3	10	10	1.5
n-Dodecane	4.3	5.5	11	8.6	13	16	21	16
TVOC	4420	4730	5950	5900	5820	1780	1300	163
%RSD								
m,p-Xylene	27	36	37	3.7	9.5	17	20	-
n-Nonane	18	25	17	0.37	1.9	4.3	7.0	-
o-Xylene	28	40	33	1.4	8.8	13	14	-
Propylcyclohexane	8.7	26	17	16	9.3	18	10	-
3- & 4-Ethyl toluene	15	33	16	12	0.20	4.2	3.8	-
1,3,5-Trimethylbenzene	10	31	13	11	2.7	0.7	5.8	-
n-Decane	10	25	4.3	16	1.6	2.4	4.6	13
2-Ethyl toluene	13	31	17	13	3.0	27	5.7	-
1,2,4-Trimethylbenzene	13	34	11	16	1.6	2.4	1.4	4.6
1,2,3-Trimethylbenzene	14	38	10	19	4.0	0.1	0.2	5.7
2-Methyldecane	9.0	29	5.6	29	1.2	12.6	8.0	13
trans-Decahydronaphthalene	5.9	34	11	19	4.0	6.9	2.3	10
n-Undecane	7.2	35	0.80	30	4.4	3.3	7.0	6.8
Pentylcyclohexane	4.8	48	16	37	2.4	3.7	0.7	4.7
n-Dodecane	12	34	1.3	31	11	1.0	6.1	1.4
TVOC	17	34	14	15	1.4	6.4	1.1	5.4

[a] Tests 5 and 6 on Table 8-1, performed using Glidden 4550-76262 Gloss:(Hyacinth). Test 5 - sample wt. 9.5 g; Test 6 - Sample wt. 8.8 g.

[b] Sampling times in hours.

[c] Below the method quantitation limit of 0.05 mg/m^3.

TABLE 8-17. RESULTS OF SINGLE CHAMBER REPEATABILITY TESTS (TESTS 5 AND 6) FOR VOC EMISSIONS FROM ALKYD PAINTS[a] - CHAMBER AIR CONCENTRATION PER GRAM OF PAINT

Compound	Chamber Air Concentrations (mg/m^3) per gram of paint							
TEST 5	T=0.65[b]	T=1.2	T=2.1	T=3.1	T=4.1	T=7.8	T=11.8	T=24.8
m,p-Xylene	12	14	10	7.2	4.2	0.47	0.047	ND[c]
n-Nonane	26	32	30	26	19	1.7	0.35	ND
o-Xylene	4.0	4.7	3.4	2.7	1.7	0.27	0.032	ND
Propylcyclohexane	9.3	11	11	11	7.4	0.71	0.23	ND
3- & 4-Ethyl toluene	5.1	6.9	6.2	6.1	4.7	1.4	0.44	ND
1,3,5-Trimethylbenzene	1.7	2.3	2.3	2.2	1.9	0.63	0.28	ND
n-Decane	40	54	59	63	57	15	9.3	0.061
2-Ethyl toluene	1.5	2.0	1.9	1.9	1.5	0.16	0.15	ND
1,2,4-Trimethylbenzene	5.3	7.4	7.2	7.4	6.1	2.1	1.1	0.020
1,2,3-Trimethylbenzene	1.4	2.1	2.1	2.2	1.9	0.94	0.52	0.026
2-Methyldecane	2.1	3.1	3.7	4.4	4.3	1.8	1.3	0.091
trans-Decahydronaphthalene	3.5	5.5	5.7	6.0	5.4	2.1	1.4	0.035
n-Undecane	6.2	11	12	14.9	15	8.2	7.8	1.5
Pentylcyclohexane	0.38	0.82	0.93	1.0	1.0	1.2	1.0	0.16
n-Dodecane	0.53	0.94	1.2	1.4	1.6	1.7	2.0	1.7
TVOC	589	817	768	764	625	205	139	18.5
TEST 6	T=0.70	T=1.2	T=2.2	T=3.2	T=4.2	T=7.9	T=11.9	T=24.9
m,p-Xylene	8.9	8.8	6.1	8.2	4.0	0.40	0.038	ND
n-Nonane	22	24	26	28	22	1.7	0.34	ND
o-Xylene	2.9	2.9	2.3	2.9	1.6	0.24	0.028	ND
Propylcyclohexane	8.9	7.9	9.1	9.6	9.2	0.59	0.21	ND
3- & 4-Ethyl toluene	4.4	4.6	5.4	5.6	5.0	1.4	0.45	ND
1,3,5-Trimethylbenzene	1.6	1.6	2.0	2.1	2.0	0.68	0.28	ND
n-Decane	37	41	60	55	63	17	11	0.055
2-Ethyl toluene	1.4	1.4	1.6	1.7	1.6	0.25	0.18	ND
1,2,4-Trimethylbenzene	4.8	4.9	6.6	6.4	6.5	2.3	1.2	0.023
1,2,3-Trimethylbenzene	1.3	1.3	1.9	1.8	1.9	1.0	0.56	0.026
2-Methyldecane	2.0	2.2	3.7	3.1	4.6	1.6	1.6	0.083
trans-Decahydronaphthalene	3.5	3.7	5.3	4.9	6.2	2.1	1.6	0.033
n-Undecane	6.1	6.8	13	10.5	15	9.3	9.3	1.5
Pentylcyclohexane	0.38	0.44	0.81	0.66	1.1	1.2	1.1	0.17
n-Dodecane	0.49	0.62	1.3	1.0	1.5	1.9	2.4	1.8
TVOC	503	538	677	671	662	203	148	18.5
%RSD								
m,p-Xylene	22.1	30.9	32.1	9.3	3.9	11.8	14.1	-
n-Nonane	12.5	19.7	11.1	5.2	7.5	1.3	1.4	-
o-Xylene	22.1	34.6	27.8	7.0	3.3	7.3	8.6	-
Propylcyclohexane	3.1	20.4	11.5	10.9	14.9	12.4	4.5	-
3- & 4-Ethyl toluene	9.8	27.6	10.6	6.6	5.4	1.4	1.8	-
1,3,5-Trimethylbenzene	4.9	25.5	7.6	5.5	2.9	4.9	0.3	-
n-Decane	4.6	19.4	1.2	10.5	7.2	8.0	10.2	7.3
2-Ethyl toluene	7.7	26.0	11.4	7.1	2.6	32.0	11.2	-
1,2,4-Trimethylbenzene	7.3	28.3	5.7	10.4	4.0	7.9	7.0	10.2
1,2,3-Trimethylbenzene	8.2	32.6	4.5	13.7	1.6	5.6	5.4	0.1
2-Methyldecane	3.4	23.6	0.0	23.7	4.4	7.0	13.5	7.1
trans-Decahydronaphthalene	0.3	28.5	5.2	13.8	9.6	1.4	7.9	4.5
n-Undecane	1.6	30.1	4.8	24.6	1.2	8.9	12.6	1.4
Pentylcyclohexane	0.7	43.3	10.1	31.2	3.2	1.9	6.3	8.6
n-Dodecane	6.7	29.1	4.2	25.7	5.9	4.6	11.6	7.0
TVOC	11	29	8.9	9.2	4.1	0.69	4.4	0

[a] Tests 5 and 6 on Table 8-1, performed using Glidden 4550-76262 Gloss:(Hyacinth). Test 5 - sample wt. 9.5 g; Test 6 - Sample wt. 8.78 g.

[b] Sampling times in hours.

[c] Below the method quantitation limit of ~0.005 mg/m^3 per gram of paint.

the more volatile components could have been emitted from the paint sample before it was placed into the chamber. To avoid this problem for additional tests, paint samples were placed into the chambers 5 minutes after application. Five minutes was selected as reasonable, since it should allow all application activities to take place without excessive delays in placing the paint sample into the chamber.

Two sets of interchamber variability tests were then performed to evaluate reproducibility of the test method across chambers. Tests 11 and 12 as shown in Table 8-1 were performed using a Glidden flat alkyd paint (Chim Cham). Air concentration data for these tests are provided in Table 8-18; air concentration data normalized per gram of paint are given in Table 8-19. Both tables give calculated %RSD values for measured air concentrations for paired samples collected during the two tests. Similar results for Test 13 and 14 are given in Tables 8-20 and 8-21. Tests 13 and 14 were performed using a Glidden semigloss alkyd paint (Sea Foam).

Data for these two sets of interchamber variability tests generally show the same trends as discussed for the single chamber repeatability tests. Variability between tests performed in different chambers is low as indicated by the low %RSD values calculated for air concentrations for paired samples. For these tests, high %RSD values are only reported at the latter time points when chamber air concentrations are very low. Measured air concentrations for all four of these tests were still relatively high (approximately 10 mg/m^3) at the end of the 24-hour test period for the least volatile components (i.e., 2-methyldecane, trans-decahydronaphthalene, n-undecane, pentylcyclohexane, and n-dodecane). This is in contrast to the concentration measurements for these same compounds measured during the single chamber repeatability tests using the gloss paint type. It is interesting to note that when the paint samples were removed from the chamber at the end of the 24-hour test period, the gloss paint samples (tests 3 and 4) were dry, whereas the flat (tests 11 and 12) and the semigloss (tests 13 and 14) paint samples were still tacky. This visual observation for the flat and semigloss paint samples is consistent with continued emission of the less volatile components reported in Tables 8-18 to 8-21.

Tests 21 and 22 (Table 8-1) were performed to evaluate the effect of surface air velocity on VOC emissions for the alkyd paints . A Sherwin Williams gloss alkyd paint (Bumbershoot) was used for these tests. Test 21 was performed using a fan inside the chamber to generate air velocities of approximately 10 cm/s across the surface of the paint

TABLE 8-18. RESULTS OF INTERCHAMBER VARIABILITY TESTS (TESTS 11 AND 12) FOR VOC EMISSIONS FROM ALKYD PAINTS[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentrations (mg/m^3)							
TEST 11	T=0.63[b]	T=1.1	T=2.1	T=3.1	T=4.1	T=8.7	T=12.7	T=24.7
m,p-Xylene	78	68	40	28	18	1.9	0.21	ND[c]
n-Nonane	37	31	25	21	15	3.2	0.84	ND
o-Xylene	20	17	11	7.2	4.9	0.71	0.10	ND
Propylcyclohexane	9.6	8.5	6.3	5.0	4.3	1.0	0.29	ND
3- & 4-Ethyl toluene	7.1	6.8	5.5	4.3	3.6	1.2	0.42	ND
1,3,5-Trimethylbenzene	2.4	2.4	2.1	1.7	1.5	0.6	0.25	ND
n-Decane	110.0	110.0	98	95	79	26	20.0	5.1
2-Ethyl toluene	2.3	2.2	1.9	1.5	1.3	0.52	0.19	ND
1,2,4-Trimethylbenzene	7.0	7.2	6.6	5.6	4.9	2.2	1.0	0.058
1,2,3-Trimethylbenzene	2.1	2.2	2.0	1.7	1.7	0.79	0.42	0.056
2-Methyldecane	40	45	44	44	43	11	11	13
trans-Decahydronaphthalene	61	67	66	60	59	18	15	5.2
n-Undecane	180	180.0	180.0	190	190	36	28	36
Pentylcyclohexane	27	31	29	27	32	8.6	8.4	9.3
n-Dodecane	31	37	38	41	43	18	17	25
TVOC	3300	3700	3400	3200	2900	1400	1200	840
TEST 12	T=0.65	T=1.2	T=2.2	T=3.2	T=4.2	T=8.7	T=12.7	T=24.7
m,p-Xylene	74	72	49	30	19	4.2	0.85	ND
n-Nonane	28	30	24	18	14	6.0	2.98	0.13
o-Xylene	20	16	12	8.3	5.4	1.6	0.40	ND
Propylcyclohexane	7.5	7.0	6.3	5.2	3.6	1.9	0.86	0.054
3- & 4-Ethyl toluene	6.3	6.0	5.3	4.1	3.4	1.9	1.0	0.11
1,3,5-Trimethylbenzene	2.0	2.0	2.0	1.5	1.3	0.78	0.52	0.090
n-Decane	86	78	86	72	64	26	22	13
2-Ethyl toluene	2.0	2.0	1.7	1.5	1.2	0.68	0.39	0.068
1,2,4-Trimethylbenzene	5.9	6.3	5.5	4.6	3.7	2.6	1.7	0.42
1,2,3-Trimethylbenzene	1.8	1.9	1.8	1.5	1.2	0.86	0.63	0.22
2-Methyldecane	32	34	36	30	28	12	11	12
trans-Decahydronaphthalene	53	59	53	47	40	20	18	12
n-Undecane	150	160	160	140	140	29	27	26
Pentylcyclohexane	18	23	25	20	20	8.6	8.8	7.7
n-Dodecane	26	30	30	28	24	16	15	16
TVOC	2400	2600	2500	2100	1800	1100	1000	790
%RSD								
m,p-Xylene	3.7	4.1	15	4.7	4.6	53	86	-
n-Nonane	19	3.2	3.0	10	6.5	43	79	-
o-Xylene	1.3	1.7	8.4	10	6.5	56	84	-
Propylcyclohexane	17	14	0.40	1.9	12	43	71	-
3- & 4-Ethyl toluene	7.6	8.6	3.2	3.4	5.1	29	58	-
1,3,5-Trimethylbenzene	13	13	4.2	9.1	12	14	49	-
n-Decane	18	21	10	19	16	0.93	7.4	60
2-Ethyl toluene	11	6.8	8.1	1.6	7.2	19	48	-
1,2,4-Trimethylbenzene	12	10	12	14	19	13	38	110
1,2,3-Trimethylbenzene	12	7.7	6.6	10	23	5.4	28	85
2-Methyldecane	17	19	15	26	30	6.3	0.91	2.3
trans-Decahydronaphthalene	9.3	9.1	15	17	28	7.1	15	57
n-Undecane	12	9.3	9.1	17	19	16	3.3	22
Pentylcyclohexane	28	20	10	20	34	0.17	2.9	13
n-Dodecane	14	15	16	27	40	7.4	8.5	29
TVOC	22	25	22	29	33	17	13	4

[a] Tests 11 and 12 on Table 8-1, performed using Glidden 5700-25312 Flat: (Chim Cham). Test 11 - Sample wt. 13.53 g; Test 12 - Sample wt. 14.83 g.

[b] Sampling times in hours.

[c] Below the method quantitation limit of 0.05 mg/m^3.

TABLE 8-19. RESULTS OF INTERCHAMBER VARIABILITY TESTS (TESTS 11 AND 12) FOR VOC EMISSIONS FROM ALKYD PAINTS[a] - CHAMBER AIR CONCENTRATION PER GRAM OF PAINT

Compound	Chamber Air Concentrations (mg/m^3) per gram of paint							
TEST 11	T=0.63[b]	T=1.1	T=2.1	T=3.1	T=4.1	T=8.7	T=12.7	T=24.7
m,p-Xylene	5.8	5.0	2.9	2.1	1.3	0.14	0.015	ND[c]
n-Nonane	2.7	2.3	1.8	1.5	1.1	0.24	0.062	ND
o-Xylene	1.5	1.2	0.81	0.53	0.37	0.05	0.007	ND
Propylcyclohexane	0.71	0.63	0.47	0.37	0.31	0.076	0.021	ND
3- & 4-Ethyl toluene	0.52	0.50	0.41	0.32	0.27	0.092	0.031	ND
1,3,5-Trimethylbenzene	0.18	0.18	0.15	0.13	0.11	0.047	0.019	0.38
n-Decane	8.1	7.8	7.2	7.0	5.9	2.0	1.5	ND
2-Ethyl toluene	0.17	0.16	0.14	0.11	0.10	0.038	0.014	0.0043
1,2,4-Trimethylbenzene	0.52	0.53	0.49	0.41	0.36	0.16	0.072	0.0
1,2,3-Trimethylbenzene	0.16	0.16	0.15	0.13	0.12	0.06	0.031	0.0041
2-Methyldecane	3.0	3.3	3.3	3.2	3.2	0.81	0.79	0.93
trans-Decahydronaphthalene	4.5	4.9	4.9	4.4	4.4	1.3	1.1	0.39
n-Undecane	13	14	14	14	14	2.7	2.1	2.7
Pentylcyclohexane	2.0	2.3	2.1	2.0	2.4	0.64	0.62	0.69
n-Dodecane	2.3	2.8	2.8	3.0	3.2	1.3	1.3	1.8
TVOC	240	270	250	240	220	100	89	62
TEST 12	T=0.65	T=1.2	T=2.2	T=3.2	T=4.2	T=8.7	T=12.7	T=24.7
m,p-Xylene	5.0	4.9	3.3	2.0	1.3	0.28	0.057	0.0051
n-Nonane	1.9	2.0	1.6	1.2	0.95	0.41	0.20	0.009
o-Xylene	1.4	1.1	0.83	0.56	0.37	0.11	0.027	ND
Propylcyclohexane	0.50	0.47	0.43	0.35	0.24	0.13	0.058	0.0037
3- & 4-Ethyl toluene	0.43	0.40	0.36	0.28	0.23	0.13	0.067	0.0072
1,3,5-Trimethylbenzene	0.14	0.13	0.13	0.10	0.08	0.05	0.035	0.0061
n-Decane	5.8	5.3	5.8	4.9	4.3	1.8	1.5	0.85
2-Ethyl toluene	0.13	0.13	0.11	0.10	0.079	0.046	0.026	0.0046
1,2,4-Trimethylbenzene	0.40	0.42	0.37	0.31	0.25	0.17	0.11	0.028
1,2,3-Trimethylbenzene	0.12	0.13	0.12	0.10	0.082	0.058	0.04	0.015
2-Methyldecane	2.1	2.3	2.4	2.0	1.9	0.81	0.73	0.82
trans-Decahydronaphthalene	3.6	4.0	3.6	3.1	2.7	1.3	1.2	0.82
n-Undecane	10	11	11	9.8	9.6	1.9	1.8	1.8
Pentylcyclohexane	1.2	1.6	1.7	1.4	1.3	0.58	0.59	0.52
n-Dodecane	1.7	2.0	2.1	1.9	1.6	1.1	1.0	1.1
TVOC	160	170	170	140	120	71	68	53
%RSD								
m,p-Xylene	10	2.4	8.7	1.8	1.9	47	82	-
n-Nonane	25	10	9.5	16	13	37	74	-
o-Xylene	5.2	8	1.9	3.9	0.067	51	80	-
Propylcyclohexane	23	20	6.1	4.6	18.7	37	66	-
3- & 4-Ethyl toluene	14	15	10	10	12	22	53	-
1,3,5-Trimethylbenzene	19	19	11	16	19	8	43	-
n-Decane	24	27	16	25	22	7	0.88	55
2-Ethyl toluene	18	13	15	8	14	13	42	-
1,2,4-Trimethylbenzene	19	16	19	21	26	6	32	104
1,2,3-Trimethylbenzene	18	14	13	16	29	1.1	21	81
2-Methyldecane	23	25	22	32	36	0.19	5.6	8.8
trans-Decahydronaphthalene	16	16	22	24	34	0.6	8.2	51
n-Undecane	18	16	16	23	26	23	10	28
Pentylcyclohexane	34	26	17	27	40	6.3	3.6	20
n-Dodecane	21	22	23	33	46	14	15	36
TVOC	28	32	27	37	42	24	18	11

[a] Tests 11 and 12 on Table 8-1, performed using Glidden 5700-25312 Flat:(Chim Cham). Sample wt - 13.53 g; sample wt - 14.83 g.
[b] Sampling time in hours.
[c] Below the method quantitation limit of ~0.005 mg/m^3 per gram of paint.

TABLE 8-20. RESULTS OF INTERCHAMBER VARIABILITY TESTS (TESTS 13 AND 14) FOR VOC EMISSIONS FROM ALKYD PAINTS[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentrations (mg/m^3)							
TEST 13	T=0.65[b]	T=1.2	T=2.2	T=3.2	T=4.2	T=8.7	T=12.7	T=24.7
m,p-Xylene	100	110	93	67	48	9.2	1.7	ND[c]
n-Nonane	130	140	120	120	91	25	11	ND
o-Xylene	31	32	28	23	16	4.5	1.0	ND
Propylcyclohexane	31	32	34	32	23	5.8	3.8	ND
3- & 4-Ethyl toluene	27	31	32	30	26	12	6.9	ND
1,3,5-Trimethylbenzene	9.1	11	11	11	8.9	4.3	3.1	0.39
n-Decane	130	150	150	150	140	34	34	18
2-Ethyl toluene	8.7	10	10	10	9	2.5	2.1	0.28
1,2,4-Trimethylbenzene	26	31	31	32	28	13	10	2.0
1,2,3-Trimethylbenzene	7.5	8.9	10	10	9	5.4	4.4	1.2
2-Methyldecane	15	21	22	26	24	11	12	11
trans-Decahydronaphthalene	25	30	32	36	33	16	16	7.2
n-Undecane	73	95	93	110	100	24	25	27
Pentylcyclohexane	7.1	10	11	11	11	7.0	8.4	6.6
n-Dodecane	10	13	15	17	16	13	16	18
TVOC	2200	2700	2600	2700	2500	1100	1060	620
TEST 14	T=0.65	T=1.2	T=2.2	T=3.2	T=4.2	T=8.7	T=12.7	T=24.7
m,p-Xylene	100	120	100	77	60	15	4.3	ND
n-Nonane	120	140	140	120	110	33	17	0.9
o-Xylene	31	37	31	23	18	6.4	2.2	0.062
Propylcyclohexane	28	34	32	29	27	7.9	5.0	0.38
3- & 4-Ethyl toluene	24	30	31	27	25	14	10	1.60
1,3,5-Trimethylbenzene	7.7	10	10	9	9	4.6	3.8	1.0
n-Decane	140	160	170	160	150	36	36	23
2-Ethyl toluene	7.5	9.5	9.5	9.3	8.2	3.1	2.7	0.83
1,2,4-Trimethylbenzene	23	29	29	27	26	13	12	4.4
1,2,3-Trimethylbenzene	6.0	8.0	8.6	8.1	7.6	5.5	4.9	2.2
2-Methyldecane	14	19	21	21	19	12	12	10
trans-Decahydronaphthalene	21	29	30	29	28	17	17	10
n-Undecane	72	94	103	97	91	26	28	23
Pentylcyclohexane	7.6	9.3	9.3	9.1	9.4	7.6	7.3	5.6
n-Dodecane	8.6	12	13	13	13	13	15	13
TVOC	2100	2400	2500	2400	2000	1090	808	550
%RSD								
m,p-Xylene	0.68	4.0	5.8	9.2	16	32	59	-
n-Nonane	4.9	1.4	6.6	1.4	13	19	32	-
o-Xylene	0.54	9.1	6.1	0.8	5	25	54	-
Propylcyclohexane	7.5	4.2	3.6	6.9	11	21	20	-
3- & 4-Ethyl toluene	8.4	2.9	3.0	7.3	1.6	8.6	25	84
1,3,5-Trimethylbenzene	12	7.8	3.8	9.3	3.3	4.5	14	64
n-Decane	6.1	3.7	6.1	4.7	4.9	3.4	3.1	16
2-Ethyl toluene	10	3.3	4.4	6.1	3.5	16	17	70
1,2,4-Trimethylbenzene	10	3.5	4.6	11	5.8	3.8	9.7	53
1,2,3-Trimethylbenzene	16	7.8	7.9	13	8.6	1.5	7.8	38
2-Methyldecane	7.6	9.0	6.1	15	18	2.3	0.66	1.7
trans-Decahydronaphthalene	13	4.0	4.6	14	11	2.1	4.0	22
n-Undecane	0.84	1.0	7.0	9.1	8.5	5.6	6.4	12
Pentylcyclohexane	4.9	3.7	8.7	16	8.9	5.3	9.4	12
n-Dodecane	11	7.5	12	18	15	4.4	3.4	22
TVOC	2.3	5.9	2.00	5.9	11	0.46	13	6.00

[a] Tests 13 and 14 on Table 8-1, performed using Glidden 8000-46212 Semigloss:(Sea Foam). Test 13 - sample wt. 11.19 g; Test 14 - Sample wt. 12.23 g.

[b] Sampling times in hours.

[c] Below the method quantitation limit of ~0.005 mg/m^3 per gram of paint.

TABLE 8-21. RESULTS OF INTERCHAMBER VARIABILITY TESTS (TESTS 13 AND 14) FOR VOC EMISSIONS FROM ALKYD PAINTS[a] - CHAMBER AIR CONCENTRATION PER GRAM OF PAINT

Compound	Chamber Air Concentrations (mg/m^3) per Gram of Paint							
TEST 13	T=0.65[b]	T=1.2	T=2.2	T=3.2	T=4.2	T=8.7	T=12.7	T=24.7
m,p-Xylene	9.1	10.0	8.3	6.0	4.3	0.82	0.16	ND[c]
n-Nonane	11	12	11	10	8.2	2.2	1.0	ND
o-Xylene	2.8	2.9	2.5	2.0	1.5	0.40	0.09	ND
Propylcyclohexane	2.8	2.9	3.0	2.8	2.1	0.52	0.34	ND
3- & 4-Ethyl toluene	2.4	2.8	2.8	2.7	2.3	1.1	0.62	0.037
1,3,5-Trimethylbenzene	0.82	1.0	0.94	1.0	0.80	0.39	0.28	0.035
n-Decane	12	14	14	14	12	3.0	3.05	1.6
2-Ethyl toluene	0.78	0.89	0.90	0.90	0.77	0.22	0.19	0.025
1,2,4-Trimethylbenzene	2.4	2.7	2.8	2.8	2.5	1.1	0.90	0.177
1,2,3-Trimethylbenzene	0.67	0.80	0.86	0.87	0.76	0.48	0.39	0.11
2-Methyldecane	1.4	1.9	2.0	2.4	2.2	1.0	1.1	1.0
trans-Decahydronaphthalene	2.2	2.7	2.9	3.2	2.9	1.5	1.4	0.639
n-Undecane	6.5	8.5	8.4	9.8	9.1	2.2	2.3	2.5
Pentylcyclohexane	0.64	0.87	0.94	1.0	0.95	0.63	0.75	0.59
n-Dodecane	0.89	1.2	1.4	1.5	1.5	1.2	1.4	1.7
TVOC	200.9	240	240	240	220	103	95	55
TEST 14	T=0.65	T=1.2	T=2.2	T=3.2	T=4.2	T=8.7	T=12.7	T=24.7
m,p-Xylene	8.4	9.7	8.2	6.3	4.9	1.2	0.35	ND
n-Nonane	9.7	12	11	9.8	8.9	2.7	1.4	0.08
o-Xylene	2.5	3.0	2.5	1.9	1.4	0.52	0.18	0.006
Propylcyclohexane	2.3	2.8	2.6	2.4	2.2	0.64	0.41	0.034
3- & 4-Ethyl toluene	2.0	2.5	2.5	2.2	2.1	1.1	0.80	0.14
1,3,5-Trimethylbenzene	0.63	0.79	0.81	0.78	0.70	0.38	0.31	0.093
n-Decane	12	13	14	13	12	2.9	2.9	2.1
2-Ethyl toluene	0.62	0.77	0.77	0.76	0.67	0.25	0.22	0.074
1,2,4-Trimethylbenzene	1.9	2.4	2.4	2.2	2.1	1.1	0.9	0.39
1,2,3-Trimethylbenzene	0.49	0.66	0.70	0.66	0.62	0.45	0.40	0.19
2-Methyldecane	1.1	1.5	1.7	1.7	1.5	1.0	1.0	0.94
trans-Decahydronaphthalene	1.7	2.3	2.5	2.4	2.3	1.4	1.4	0.88
n-Undecane	5.9	7.7	8.4	7.9	7.4	2.1	2.3	2.1
Pentylcyclohexane	0.62	0.76	0.76	0.74	0.77	0.62	0.60	0.50
n-Dodecane	0.70	1.0	1.1	1.1	1.1	1.0	1.2	1.2
TVOC	170	200	200	190	160	89	66	45
%RSD								
m,p-Xylene	5.6	2.3	0.51	3.0	9.4	26	54	NC
n-Nonane	11	4.9	0.29	4.8	6.4	13	26	NC
o-Xylene	6.8	2.8	0.21	5.5	1.3	19	48	NC
Propylcyclohexane	14	2.1	10	13	4.6	15	14	NC
3- & 4-Ethyl toluene	15	9.2	9.3	14	7.9	2.3	18	80
1,3,5-Trimethylbenzene	18	14	10	16	10	1.7	7.5	59
n-Decane	0.23	2.5	0.23	1.6	1.4	2.9	3.1	10
2-Ethyl toluene	17	10	11	12	10	10	11	65
1,2,4-Trimethylbenzene	16	10	11	17	12	2.5	3.4	48
1,2,3-Trimethylbenzene	22	14	14	19	15	4.7	1.5	32
2-Methyldecane	14	15	12	21	24	4.0	5.6	8
trans-Decahydronaphthalene	19	10	11	20	18	4.2	2.3	16
n-Undecane	7.1	7.2	0.68	12	15	0.73	0.12	18
Pentylcyclohexane	1.4	10	15	22	15	1.0	16	18
n-Dodecane	17	14	18	25	21	11	10	28
TVOC	8.6	9.1	8.6	12	16	7.3	18	10.0

[a] Tests 13 and 14 on Table 8-1, performed using Glidden 8000-46212 Semigloss:(Sea Foam). Sample wt - 11.19 g; Sample wt. (12.23 g)

[b] Sampling times in hours.

[c] Below the method quantitation limit of ~0.005 mg/m^3 per gram of paint.

samples. Test 22 was performed without the fan. Air velocities across the paint surface for this test were less than 2 cm/s. Results for these two tests are given in Table 8-22 for chamber air concentrations and in Table 8-23 for chamber air concentrations normalized per gram of paint. Results for Test 21 with the fan show higher air concentrations at the earlier time points with a more rapid decrease in air concentrations over time when compared to results for Test 22 without the fan. In the absence of a fan the least volatile components still show relatively high chamber air concentration at the end of the 24-hour test period.

8.3.4 SVOC Emissions from Latex Paint Samples

As with the alkyd paints, a range finding test (Test 1, Table 8-1) was performed for tests with a latex paint sample to determine the experimental conditions for all subsequent small chamber tests. This test was performed using a Sherwin Williams flat paint (Marmalade). Results for this test are given in Tables 8-24 and 8-25 as chamber air concentrations and chamber air concentrations normalized per gram of paint. Results show a slow increase in air concentrations over time followed by a gradual decrease. For most of the SVOCs, highest chamber air concentrations were measured between 24 and 96 hours after application. Very high concentrations (>150 mg/m^3) were measured for ethylene glycol. Based on the results of this test several modifications were made in the test procedure.

- Smaller samples (0.5 L) were collected in order to keep analyte masses within the dynamic range of the test method.
- Samples were collected at 1, 12, 24, 48, 96, 120, and 168 hours to more fully characterize the SVOC emissions over time.

All subsequent emissions tests were performed using these modifications.

Single chamber repeatability and interchamber variability tests were performed to evaluate the reproducibility of the small chamber emissions test for latex paint samples under carefully controlled conditions. For the latex paints, single chamber repeatability tests were Tests 3 and 4 and Tests 17 and 18 as shown in Table 8-1. Tests 3 and 4 were performed using a Sherwin Williams flat paint (Marmalade). Tests 17 and 18 were performed using a Glidden semigloss paint (Down Yonder). Interchamber variability tests are Tests 15 and 16 in Table 8-1. Tests 15 and 16 were performed using a Sherwin Williams gloss paint (Rose Dawn). Results for these six test are presented in Tables 8-26 to 8-31. Data for diethylene glycol has been included in these tables to provide some information on its behavior during emissions tests. However, these data should only be considered estimates since the method

TABLE 8-22. RESULTS OF AIR VELOCITY TESTS (TESTS 21 AND 22) ON VOC EMISSIONS FROM ALKYD PAINTS[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentrations (mg/m3)							
TEST 21 (FAN)	T=.67[b]	T=1.2	T=2.2	T=3.2	T=4.2	T=8.2	T=12.7	T=24.7
m,p-Xylene	145	120	68	40	24	1.4	ND[c]	ND
n-Nonane	420	410	280	200	130	8.7	0.47	ND
o-Xylene	25	25	14	9.3	5.4	0.46	ND	ND
Propylcyclohexane	120	120	80	59	38	3.3	0.22	ND
3- & 4-Ethyl toluene	10	8.6	6.8	5.5	4.1	0.74	0.090	ND
1,3,5-Trimethylbenzene	3.0	4.6	4.2	3.1	2.5	0.57	0.089	ND
n-Decane	540	540	570	500	470	89	21	0.25
2-Ethyl toluene	2.8	2.7	2.0	1.8	1.3	0.29	ND	ND
1,2,4-Trimethylbenzene	12	12	11	10	7.6	2.2	0.42	ND
1,2,3-Trimethylbenzene	3.0	3	3.1	2.7	2.2	0.83	0.24	ND
2-Methyldecane	50	57	64	65	69	33	12	0.15
trans-Decahydronaphthalene	70	78	77	73	63	23	6.0	0.067
n-Undecane	220	270	300	290	370	110	78	2.7
Pentylcyclohexane	16	17	22	26	28	24	13	0.45
n-Dodecane	27	33	38	46	50	57	55	14
TVOC	7700	7400	6400	5700	5000	1800	860	68
TEST 22 (NO FAN)	T=.67	T=1.2	T=2.2	T=3.2	T=4.2	T=8.2	T=12.7	T=24.7
m,p-Xylene	90	100	81	56	40	6.3	0.88	ND
n-Nonane	210	260	250	210	170	47	14	ND
o-Xylene	16	18	15	11	8.8	1.8	0.34	ND
Propylcyclohexane	52	68	70	55	47	15	5.3	ND
3- & 4-Ethyl toluene	4.0	5	5.0	4.3	4.0	2.0	0.88	ND
1,3,5-Trimethylbenzene	1.7	2	2.5	2.2	2.1	1.2	0.66	ND
n-Decane	220	310	300	290	290	110	100	4.7
2-Ethyl toluene	1.1	1.3	1.3	1.2	1.1	0.63	0.35	ND
1,2,4-Trimethylbenzene	4.7	6.1	6.8	6.6	5.9	3.7	2.4	0.087
1,2,3-Trimethylbenzene	1.1	1.4	1.6	1.6	1.4	1.0	0.86	0.070
2-Methyldecane	13	19	24	23	25	24	27	7.0
trans-Decahydronaphthalene	24	33	37	35	37	25	22	2.3
n-Undecane	60	81	99	119	130	74	83	67
Pentylcyclohexane	3.8	6.4	7.3	7.9	8.8	10	13	10
n-Dodecane	6.2	8.9	11	13	13	17	23	46
TVOC	2800	3600	3600	3400	3100	1800	1400	520

[a] Tests 21 & 22 on Table 8-1, performed using Sherwin Williams-1435 Gloss: (Bumbershoot): Test 21 - sample wt (7.09 g): Test 22 - sample wt (7.56 g).

[b] Sampling time in hours.

[c] Below the method quantitation limit.

TABLE 8-23. RESULTS OF AIR VELOCITY TESTS (TESTS 21 AND 22) ON VOC EMISSIONS FROM ALKYD PAINTS[a] - CHAMBER AIR CONCENTRATION PER GRAM OF PAINT

Compound	Chamber Air Concentrations (mg/m^3) per Gram of Paint							
TEST 21 (FAN)	T=.67[b]	T=1.2	T=2.2	T=3.2	T=4.2	T=8.2	T=12.7	T=24.7
m,p-Xylene	20	17	9.6	5.6	3.3	0.19	ND[c]	ND
n-Nonane	59	58	39	28	18	1.2	0.066	ND
o-Xylene	3.5	3.5	2.0	1.3	0.76	0.065	ND	ND
Propylcyclohexane	16	16	11	8.3	5.4	0.47	0.031	ND
3- & 4-Ethyl toluene	1.3	1.2	1.0	0.78	0.58	0.10	0.013	ND
1,3,5-Trimethylbenzene	0.42	0.65	0.59	0.43	0.35	0.080	0.013	ND
n-Decane	76	75	80	70	66	13	3.0	0.035
2-Ethyl toluene	0.39	0.37	0.29	0.26	0.19	0.041	ND	ND
1,2,4-Trimethylbenzene	1.7	1.7	1.6	1.4	1.1	0.31	0.059	ND
1,2,3-Trimethylbenzene	0.42	0.46	0.43	0.38	0.31	0.12	0.034	ND
2-Methyldecane	7.1	8.1	9.1	9.1	9.7	4.6	1.7	0.021
trans-Decahydronaphthalene	10	11	11	10	8.9	3.2	0.85	0.0095
n-Undecane	30	39	42	41	52	16	11	0.38
Pentylcyclohexane	2.3	2.4	3.2	3.6	3.9	3.4	1.8	0.064
n-Dodecane	3.8	4.6	5.3	6.5	7.1	8.1	7.8	2.0
TVOC	1100	1000	900	800	700	260	120	10
TEST 22 (NO FAN)	T=.67	T=1.2	T=2.2	T=3.2	T=4.2	T=8.2	T=12.7	T=24.7
m,p-Xylene	12	13	11	7.4	5.3	0.83	0.12	ND
n-Nonane	28	34	33	27	23	6.2	1.8	ND
o-Xylene	2.1	2.4	2.0	1.5	1.2	0.24	0.045	ND
Propylcyclohexane	6.9	9.0	9.2	7.3	6.2	2.0	0.70	ND
3- & 4-Ethyl toluene	0.53	0.66	0.66	0.57	0.53	0.27	0.12	ND
1,3,5-Trimethylbenzene	0.23	0.32	0.33	0.29	0.28	0.16	0.087	ND
n-Decane	29	41	40	38	38	14	13	0.62
2-Ethyl toluene	0.15	0.17	0.17	0.16	0.15	0.083	0.046	ND
1,2,4-Trimethylbenzene	0.62	0.81	0.89	0.87	0.78	0.50	0.31	0.012
1,2,3-Trimethylbenzene	0.15	0.19	0.21	0.21	0.19	0.14	0.11	0.0093
2-Methyldecane	1.7	2.5	3.2	3.0	3.4	3.2	3.6	0.93
trans-Decahydronaphthalene	3.2	4.4	4.9	4.6	4.8	3.3	2.9	0.31
n-Undecane	8.0	11	13	16	17	9.7	11	8.9
Pentylcyclohexane	0.50	0.85	1.0	1.0	1.2	1.3	1.7	1.4
n-Dodecane	0.82	1.2	1.4	1.7	1.8	2.2	3.1	6.1
TVOC	370	480	470	450	410	240	190	70

[a] Tests 21 and 22 on Table 8-1, performed using Sherwin Williams-1435 Gloss:(Bumbershoot). Test 21 Sample wt - 7.09 g; Test 22 sample wt. (7.56 g).

[b] Sampling time in hours.

[c] Below the method quantitation limit of ~0.05 mg/m^3 per g of paint.

TABLE 8-24. RESULTS OF RANGE FINDING TEST (TEST 1) FOR SVOC EMISSIONS FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentrations (mg/m^3)					
TEST 1	T=8.7[b]	T=24.7	T=48.7	T=72.7	T=96.7	T=120.7
Ethylene glycol	37	176	164	169	164	57
1,2-Propanediol	3.9	13	10	9.0	7.1	1.9
o-Xylene	ND[c]	ND	ND	ND	ND	ND
2-(2-Methoxyethoxy)ethanol	ND	ND	ND	ND	ND	ND
Diethylene glycol	0.052	0.70	0.068	1.7	2.2	1.4
Dipropylene glycol	0.043	0.30	0.19	0.40	0.48	0.29
2-(2-Butoxyethoxy)ethanol	2.5	5.4	4.2	4.4	4.1	1.6
2-(2-Butoxyethoxy)ethyl acetate	0.0060	ND	ND	ND	ND	ND
Texanol	9.3	16	11	12	10	4.3
TVOC	53	210	190	190	190	66

[a] Test 1 on Table 8-1 performed using Sherwin Williams 1629 Flat:(Marmalade). Sample Wt. - (11.18g).
[b] Sampling times in hours.
[c] Below the method quantitation limit.

TABLE 8-25. RESULTS OF RANGE FINDING TEST (TEST 1) FOR SVOC EMISSIONS FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATION PER GRAM OF PAINT

Compound	Chamber Air Concentration (mg/m^3) per Gram of Paint					
TEST 1	T=8.7[b]	T=24.7	T=48.7	T=72.7	T=96.7	T=120.7
Ethylene glycol	3.3	16	15	15	15	5.1
1,2-Propanediol	0.35	1.1	0.94	0.80	0.63	0.17
o-Xylene	ND[c]	ND	ND	ND	ND	ND
2-(2-Methoxyethoxy)ethanol	ND	ND	ND	ND	ND	ND
Diethylene glycol	0.0046	0.062	0.0061	0.15	0.20	0.13
Dipropylene glycol	0.0038	0.027	0.017	0.036	0.043	0.026
2-(2-Butoxyethoxy)ethanol	0.22	0.48	0.38	0.40	0.37	0.14
2-(2-Butoxyethoxy)ethyl acetate	0.00053	ND	ND	ND	ND	ND
Texanol	0.83	1.4	1.0	1.1	0.93	0.38
TVOC	4.7	19	17	17	17	5.9

[a] Test 1 on Table 8-1 performed using Sherwin Williams 1629 Flat:(Marmalade). Sample Wt. - (11.18g).
[b] Sampling times in hours.
[c] Below the method quantitation limit.

TABLE 8-26. RESULTS OF SINGLE CHAMBER REPEATABILITY TESTS (TESTS 3 AND 4) FOR SVOC EMISSIONS FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentration (mg/m^3)						
TEST 3	T=1.2[b]	T=12.2	T=24.2	T=49.0	T=96.5	T=120	T=168
1,2-Propanediol	ND[c]	2.0	8.1	SL	4.2	2.0	1.1
Ethylene glycol	ND	9.2	64	SL	73	31	29
2-(2-Butoxyethoxy)ethanol	ND	1.5	2.7	SL	1.8	0.65	0.89
Texanol	13	14	12	SL	8.1	3.9	5.8
Diethylene glycol[e]	ND	ND	ND	SL	0.79	0.71	1.6
TVOC	13	27	87	-	88	38	38
TEST 4	T=1.3	T=12.2	T=24.2	T=48.3	T=96.2	T=120	T=170
1,2-Propanediol	ND	2.6	SL	7.5	3.3	2.3	0.72
Ethylene glycol	ND	12	SL	88	44	40	20
2-(2-Butoxyethoxy)ethanol	ND	1.6	SL	2.6	1.4	1.3	0.77
Texanol	16	14	SL	13	6.8	5.9	4.3
Diethylene glycol	ND	ND	SL	0.76	0.65	1.1	1.2
TVOC	16	30	-	111	56	51	27
% RSD							
1,2-Propanediol	-	20	-	-	17	10	27
Ethylene glycol	-	20	-	-	35	20	26
2-(2-Butoxyethoxy)ethanol	-	3.6	-	-	17	45	11
Texanol	18	2.3	-	-	12	29	22
Diethylene glycol	-	-	-	-	14	30	21
TVOC	18	7.4	-	-	31	21	24

[a]Tests 3 and 4 on Table 8-1, performed using Sherwin Williams 1629 Flat (Marmalade); Test 3 - sample wt (12.74 g); Test 4 - sample wt (11.8 g).
[b]Sampling time in hours.
[c]Below the method quantitation limit - see Table 8-10.
[d]Sample lost.
[e]Results reported for information, due to poor method performance results should only be considered semiquantitative.

TABLE 8-27. RESULTS OF SINGLE CHAMBER REPEATABILITY TESTS (TESTS 3 AND 4) FOR SVOC EMISSIONS FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATION PER GRAM OF PAINT

Compound	Chamber Air Concentration (mg/m^3) per Gram of Paint						
TEST 3	T=1.2[b]	T=12.2	T=24.2	T=49.0	T=96.5	T=120	T=168
1,2-Propanediol	ND[c]	0.15	0.63	SL[d]	0.33	0.16	0.084
Ethylene glycol	ND	0.72	5.0	SL	5.7	2.4	2.3
2-(2-Butoxyethoxy)ethanol	ND	0.12	0.21	SL	0.14	0.05	0.07
Texanol	0.99	1.1	0.94	SL	0.63	0.31	0.46
Diethylene glycol[e]	ND	ND	ND	SL	0.062	0.056	0.13
TVOC	0.99	2.1	6.8	SL	6.9	3.0	3.0
TEST 4	T=1.3	T=12	T=24	T=48	T=96	T=120	T=170
1,2-Propanediol	ND	0.22	SL	0.64	0.28	0.20	0.061
Ethylene glycol	ND	1.0	SL	7.5	3.7	3.4	1.7
2-(2-Butoxyethoxy)ethanol	ND	0.14	SL	0.22	0.12	0.11	0.065
Texanol	1.4	1.2	SL	1.1	0.58	0.50	0.36
Diethylene glycol	ND	ND	SL	0.065	0.055	0.092	0.010
TVOC	1.4	2.6	SL	9.5	4.7	4.3	2.2
%RSD							
1,2-Propanediol	-	25.0	-	-	11.5	15.4	22.2
Ethylene glycol	-	25.4	-	-	29.7	24.9	20.4
2-(2-Butoxyethoxy)ethanol	-	9.0	-	-	11.2	50.1	5.1
Texanol	23	3.1	-	-	6.9	34.3	16.3
Diethylene glycol	-	-	-	-	8.1	35	16
TVOC	23	15	-	-	27	25	23

[a]Tests 3 and 4 on Table 8-1, performed using Sherwin Williams 1629 Flat (Marmalade); Test 3 - sample wt (12.74 g); Test 4 - sample wt (11.8 g).
[b]Sampling time in hours.
[c]Below the method quantitation limit - see Table 8-10.
[d]Sample lost.
[e]Results reported for information, due to poor method performance results should only be considered semiquantitative.

TABLE 8-28. RESULTS OF INTERCHAMBER VARIABILITY TESTS (TESTS 15 AND 16) FOR SVOC EMISSIONS FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentration (mg/m^3)						
TEST 15	T=1 h[b]	T=12 h	T=24 h	T=48 h	T=96 h	T=120 h	T=168 h
1,2-Propanediol	ND[c]	ND	ND	SL[d]	ND	ND	ND
Ethylene glycol	ND	30	74	SL	0	53	31
2-(2-Butoxyethoxy)ethanol	14	27	29	SL	23	20	16
Texanol	2.2	1.9	1.6	SL	1.2	1.1	0.78
Diethylene glycol[e]	ND	ND	0.14	SL	ND	ND	0.39
TVOC	16	59	100	SL	24	74	48
TEST 16	T=1 h	T=12 h	T=24 h	T=48 h	T=96 h	T=120 h	T=168 h
1,2-Propanediol	ND	0.50	SL	ND	ND	ND	ND
Ethylene glycol	ND	34	SL	150	60	59	32
2-(2-Butoxyethoxy)ethanol	13	28	SL	57	23	23	17
Texanol	2.1	1.9	SL	3.3	1.2	1.3	0.81
Diethylene glycol	ND	ND	SL	0.35	ND	ND	0.21
TVOC	15	64	SL	210	84	83	50
%RSD							
1,2-Propanediol	-	-	-	-	-	-	-
Ethylene glycol	-	8.0	-	-	0.95	8.0	2.4
2-(2-Butoxyethoxy)ethanol	6.7	3.5	-	-	0.29	9.3	2.2
Texanol	3.2	2.6	-	-	2.2	10	2.7
Diethylene glycol	-	-	-	-	-	-	42
TVOC	4.6	5.7	-	-	79	7.6	2.9

[a]Sherwin Williams 200-1604 Gloss:(Rose Dawn); Test 15 - sample wt. (10.79 g); Test 16 - sample wt. (10.48 g).
[b]Nominal sampling times.
[c]Below the method quantitation limit - see Table 8-10.
[d]Sample lost.
[e]Results reported for information, due to poor method performance results should only be considered semiquantitative.

Table 8-29. RESULTS OF INTERCHAMBER VARIABILITY TESTS (TESTS 15 AND 16) FOR SVOC EMISSIONS FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATION PER GRAM OF PAINT

Compound	Chamber Air Concentration (mg/m^3) per Gram of Paint						
TEST 15	T=1 h[b]	T=12 h	T=24 h	T=48 h	T=96 h	T=120 h	T=168 h
1,2-propanediol	ND[c]	ND	ND	SL[d]	ND	ND	ND
Ethylene glycol	ND	2.8	6.9	SL	5.5	4.9	2.9
2-(2-Butoxyethoxy)ethanol	1.3	2.5	2.7	SL	2.1	1.9	1.5
Texanol	0.20	0.17	0.15	SL	0.12	0.10	0.072
Diethylene glycol[e]	ND	ND	0.013	SL	ND	ND	0.036
TVOC	1.5	5.5	9.8	SL	7.7	6.9	4.5
TEST 16	T=1 h	T=12 h	T=24 h	T=48 h	T=96 h	T=120 h	T=168 h
1,2-propanediol	ND	0.048	SL	ND	ND	ND	ND
Ethylene glycol	ND	3.2	SL	14	5.8	5.6	3.1
2-(2-Butoxyethoxy)ethanol	1.2	2.7	SL	5.5	2.2	2.2	1.6
Texanol	0.20	0.18	SL	0.31	ND	ND	ND
Diethylene glycol	ND	ND	SL	0.033	ND	ND	ND
TVOC	1.4	6.1	SL	20	8.0	7.8	4.7
%RSD							
1,2-propanediol	-	-	-	-	-	-	-
Ethylene glycol	-	10	-	-	3.0	10	4.5
2-(2-Butoxyethoxy)ethanol	4.6	5.6	-	-	1.8	11	4.2
Texanol	1.7	4.7	-	-	0	12	5.2
Diethylene glycol	-	-	-	-	-	-	40
TVOC	4.9	7.3	-	-	2.7	8.7	3.1

[a]Sherwin Williams 200-1604 Gloss:(Rose Dawn); Test 15 - sample wt. (10.79 g); Test 16 - sample wt. (10.48 g).
[b]Nominal sampling times.
[c]Below the method quantitation limit - see Table 8-10.
[d]Sample lost.
[e]Results reported for information, due to poor method performance results should only be considered semiquantitative.

TABLE 8-30. RESULTS OF SINGLE CHAMBER REPEATABILITY TESTS (TESTS 17 AND 18) FOR SVOC EMISSIONS FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentration (mg/m^3)						
TEST 17	T=1 h[b]	T=13 h	T=24 h	T=48 h	T=96 h	T=120 h	T=168 h
1,2-Propanediol	32	180	220	190	39	3	ND[c]
Ethylene glycol	6.3	57	79	81	39	4.9	ND
2-(2-Butoxyethoxy)ethanol	8.8	11	15	13	11	6.3	2.4
Texanol	31	17	23	18	14	10	7.4
Diethylene glycol	ND	ND	ND	ND	ND	ND	ND
TVOC	78	270	340	300	100	19	2.4
TEST 18	T=1.3 h	T=12.3 h	T=24.3 h	T=48.3 h	T=96.3 h	T=120 h	T=168.3 h
1,2-Propanediol	21	180	210	150	47	10	0.15
Ethylene glycol	3.9	53	69	61	40	4.9	ND
2-(2-Butoxyethoxy)ethanol	6.5	12	12	10	8.9	10	5.7
Texanol	25	19	18	13	11	13	ND
Diethylene glycol	ND	ND	ND	ND	ND	ND	ND
TVOC	56	260	310	230	110	33	2.5
% RSD							
1,2-Propanediol	30	1	4	19	14	79	-
Ethylene glycol	33	5	9	19	3	71	-
2-(2-Butoxyethoxy)ethanol	21	5	16	22	18	32	3
Texanol	15	6	19	22	18	19	-
Diethylene glycol	-	-	-	-	-	-	-
TVOC	23	2.7	6.8	19	2.7	38	2.9

[a]Glidden 64984 Semigloss:(Down Yonder); Test 17 - sample wt (7.12 g); Test 18 - sample Wt (8.29 g).
[b]Nominal sampling times. Actual times for Test 17 were 1, 13, 24, 48, 96, 120, 168.
Actual times for Test 18 were 1.3, 12.3, 24.3, 48.3, 96.3, 120.3, 168.3.
[c]Below the method quantitation limit - see Table 8-10.

TABLE 8-31. RESULTS OF SINGLE CHAMBER REPEATABILITY TESTS (TESTS 17 AND 18) FOR SVOC EMISSIONS FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATION PER GRAM OF PAINT

Compound	Chamber Air Concentration (mg/m^3) per Gram of Paint						
TEST 17	T=1 h[b]	T=13 h	T=24 h	T=48 h	T=96 h	T=120 h	T=168 h
1,2-propanediol	4.5	26	31	27	5.5	0.41	ND[c]
Ethylene glycol	0.88	8.0	11	11	5.4	0.69	ND
2-(2-Butoxyethoxy)ethanol	1.2	1.6	2.2	1.8	1.6	0.89	0.34
Texanol	4.3	2.4	3.3	2.5	1.9	1.4	1.0
Diethylene glycol	ND	ND	ND	ND	ND	ND	ND
TVOC	11	38	48	42	14	2.7	0.34
TEST 18	T=1 h	T=12 h	T=24 h	T=48 h	T=96 h	T=120 h	T=168 h
1,2-Propanediol	2.5	22	25	18	5.7	1.2	0.018
Ethylene glycol	0.47	6.4	8.4	7.4	4.8	1.8	ND
2-(2-Butoxyethoxy)ethanol	0.79	1.4	1.5	1.2	1.1	1.2	0.28
Texanol	3.0	2.3	2.1	1.5	1.3	1.6	0.69
Diethylene glycol	ND	ND	ND	ND	ND	ND	ND
TVOC	6.8	32	37	28	13	5.8	0.30
%RSD							
1,2-Propanediol	40	12	14	29	3.0	69	-
Ethylene glycol	43	16	20	30	8.2	63	-
2-(2-Butoxyethoxy)ethanol	31	5.7	26	32	28	22	14
Texanol	26	4.6	29	32	29	7.9	28
Diethylene glycol	-	-	-	-	-	-	-
TVOC	33	12	18	28	5.2	52	8.3

[a]Glidden 64984 Semigloss: (Down Yonder); Test 17 - sample wt (7.12 g); Test 18 - sample wt (8.29 g).
[b]Nominal sampling times.
[c]Below the method quantitation limit - see Table 8-10.

performance data for diethylene glycol was poor. For each test, results are presented both as chamber air concentrations and chamber air concentrations per gram of paint. To evaluate the variability between test methods, %RSD values have been calculated for measured air concentrations for paired samples from each test. Several observations can be made from the data in Tables 8-26 to 8-31.

- Reproducibility between paired tests both within a single chamber and across chambers was generally good (%RSD values >30).
- Greatest variability between paired samples was generally found when air concentrations were low.
- For all paint types, measured air concentration for ethylene glycol were high (>60 mg/m3).
- For the Glidden semigloss paint (Tests 17 and 18), air concentration for 1,2-propane diol were very high (>200 mg/m3).
- Chamber air concentration for target SVOCs gradually increased over time with highest concentrations measured at either 24 or 48 hours. After that time, concentrations showed a gradual decrease.
- For the Glidden semigloss paint (Tables 8-30 and 8-31), all target SVOCs were at relatively low concentrations at the end of the 168-hour test period with only 2-(2-butoxyethoxy)ethanol at measurable levels. In contrast, relatively high concentrations of ethylene glycol were still present in the chamber air samples for the Sherwin Williams flat paint (Tables 8-26 and 8-27) and the Sherwin Williams gloss paint (Tables 8-28 and 8-29).

A final set of comparison tests were performed (Test 19 and 20 on Table 8-1) to evaluate the effect of air surface velocity on SVOC emissions from paint samples. A Sherwin Williams flat paint (Marmalade) was used for these tests. Test 19 was performed using a fan inside the chamber to generate air velocities of approximately 10 cm/s across the surface of the paint samples. Test 20 was performed without the fan. Air velocities across the paint surface for this test were less than 2 cm/s. Results for these two tests are given in Table 8-32

TABLE 8-32. EFFECTS OF AIR VELOCITY ON SVOC EMISSIONS FROM LATEX PAINT (TESTS 19 AND 20)[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentration (mg/m^3)						
TEST 19	T=1.3[b]	T=12.3	T=24.3	T=48.3	T=96.3	T=120	T=168
1,2-Propanediol	0.38	7.7	7.1	3.1	0.57	ND[c]	ND
Ethylene glycol	ND	61	67	41	20	8.2	ND
2-(2-Butoxyethoxy)ethanol	0.89	2.7	2.5	1.4	0.75	0.43	ND
Texanol	14.6	12	10	6.4	4.0	2.9	ND
Diethylene glycol[d]	0.031	0.12	0.24	0.28	1.2	1.1	1.3
TVOC	18	83	87	52	26	13	4.1
TEST 20	T=1.3	T=12.3	T=24.3	T=48.3	T=96.3	T=120	T=168
1,2-Propanediol	ND	5.1	6.2	4.0	1.8	1.0	ND
Ethylene glycol	ND	38	57	44	33	27	8.5
2-(2-Butoxyethoxy)ethanol	0.46	2.2	2.2	1.6	1.1	0.84	0.49
Texanol	11.8	10	9.1	6.9	4.9	4.6	3.3
Diethylene glycol[d]	0.033	0.093	0.26	0.35	0.68	0.7	1.1
TVOC	14	55	75	57	41	34	14

[a]Tests 19 and 20 on Table 8-1, performed using Sherwin Williams 1629 Flat (Marmalade); Test 19 - sample wt (9.13 g); Test 20 - sample wt (10.6 g).
[b]Sampling time in hours.
[c]Below the method quantitation limit.
[d]Results reported for information, due to poor method performance results should only be considered semiquantitative.

for chamber air concentrations and in Table 8-33 for chamber air concentrations normalized per gram of paint. Results for Test 19 with the fan showed higher air concentrations at the earlier time points with a more rapid decrease in air concentrations over time when compared to results for Test 20 without the fan.

8.3.5 Aldehyde Emissions from Paint Samples

Based on information provided by the EPA, acetaldehyde and formaldehyde have been measured in emissions from polyvinyl acetate latex paints (10). Thus in order to address all of the important emissions components, a method for measuring aldehyde emissions from paints during small chamber tests was also evaluated. Testing for aldehyde emissions was performed at the same time as the emissions testing for VOCs and SVOCs from alkyd and latex paints. For Tests 1 to 20 shown in Table 8-1, samples were also collected for the analysis of aldehydes in chamber air. Samples from selected chamber tests were then analyzed based on the results of the range finding tests. Although only formaldehyde and acetaldehyde have been reported in paint emissions, acrolein, propionaldehyde, and benzaldehyde were added to the list of target analytes since the analytical method allows simultaneous determinations of a range of aldehydes. As shown in Table 8-14, acrolein was not recovered from method controls thus data for this chemical has not been reported here.

During the range finding tests for the latex paint (Test 1) and the alkyd paint (Test 2) screening analysis was performed for the aldehydes target in collected chamber air samples. Although these analyses did not allow the quantitation of aldehyde emissions, they did indicate the presence of formaldehyde and acetaldehyde in the chamber air samples during testing. It also appeared that the emissions from the latex paint sample were higher than the emissions from the alkyd paint sample. Based on these results, quantitative analysis of aldehyde emissions were performed for all of the tests for the latex paints and for both sets of interchamber variabilty tests (Tests 11 to 14) for the alkyd paints.

Data for aldehyde emissions from the single chamber repeatability tests (Tests 3 and 4, Tests 15 and 16) and the interchamber variability tests (Tests 17 and 18) for the latex paints are provided in Tables 8-34 to 8-36. Each table gives measured chamber air concentrations for samples collected at each time point for the paired tests. The variability of the measured concentrations between tests is presented as the %RSD for air samples collected at the same time point for each of the paired tests. Results of all tests show relatively high emissions for

TABLE 8-33. EFFECTS OF AIR VELOCITY ON SVOC EMISSIONS FROM LATEX PAINT (TESTS 19 AND 20)[a] - CHAMBER AIR CONCENTRATION PER GRAM OF PAINT

Compound	Chamber Air Concentration (mg/m^3) per Gram of Paint						
TEST 19	T=1.3[b]	T=12.3	T=24.3	T=48.3	T=96.3	T=120	T=168
1,2-propanediol	0.042	0.84	0.77	0.34	0.062	ND[c]	ND
Ethylene glycol	ND	6.6	7.2	4.5	2.2	0.90	ND
2-(2-butoxyethoxy)ethanol	0.10	0.29	0.27	0.15	0.082	0.047	ND
Texanol	1.60	1.30	1.1	0.70	0.44	0.32	ND
Diethylene glycol[d]	0.003	0.013	0.026	0.031	0.13	0.12	0.14
TVOC	1.9	9.0	9.4	5.7	2.9	1.4	0.44
TEST 20	T=1.3	T=12.3	T=24.3	T=48.3	T=96.3	T=120	T=168
1,2-propanediol	ND	0.48	0.59	0.38	0.17	0.094	ND
Ethylene glycol	ND	3.6	5.4	4.1	3.1	2.6	0.80
2-(2-butoxyethoxy)ethanol	0.043	0.21	0.20	0.15	0.10	0.080	0.046
Texanol	1.1	0.96	0.86	0.65	0.46	0.43	0.31
Diethylene glycol[d]	0.003	0.088	0.024	0.033	0.064	0.068	0.10
TVOC	1.3	5.3	7.1	5.3	3.9	3.3	1.3

[a]Tests 19 and 20 on Table 8-1 performed using Sherwin Williams 1629 Flat (Marmalade); Test 19 - sample wt (9.13 g); Test 20 - sample wt (10.6 g).
[b]Sampling time in hours
[c]Below the method quantitation limit.
[d]Results reported for information, due to poor method performance results should only be considered semiquantitative.

TABLE 8-34. RESULTS OF SINGLE CHAMBER REPEATABILITY TESTS (TESTS 3 AND 4) FOR ALDEHYDE EMISSIONS FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentration (µg/m^3)						
TEST 3	T=1.2[b]	T=12.2	T=24.2	T=49.0	T=96.5	T=120	T=168
Formaldehyde	59	67	15	6.5	5.0	3.9	4.4
Acetaldehyde	542	26	21	14	7.4	7.4	7.5
Propionaldehyde	ND[c]	ND	ND	ND	ND	ND	ND
Benzaldehyde	ND	ND	INT[d]	ND	ND	ND	ND
TEST 4	T=1.2	T=12.2	T=24.2	T=49.0	T=96.5	T=120	T=168
Formaldehyde	64	70	10	4.8	3.7	3.2	2.4
Acetaldehyde	329	25	16	9.0	7.5	6.5	4.8
Propionaldehyde	ND	ND	ND	ND	ND	ND	ND
Benzaldehyde	32	ND	ND	ND	ND	ND	2.2
%RSD							
Formaldehyde	5.3	3.6	26	21	21	14	41
Acetaldehyde	35	1.1	18	30	0.95	9.1	31
Propionaldehyde	-	-	-	-	-	-	-
Benzaldehyde	-	-	-	-	-	-	-

[a]Tests 3 and 4 on Table 8-1, performed using Sherwin Williams 1629 Flat (Marmalade); Test 3 - sample wt (12.74 g); Test 4 - sample wt (11.8 g).
[b]Sampling time in hours.
[c]Below the method quantitation limit - see Table 8-13.
[d]Interferent in extract prevented quantitation.

TABLE 8-35. RESULTS OF INTERCHAMBER VARIABILITY TESTS (TESTS 15 AND 16) FOR ALDEHYDE EMISSIONS FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentration (µg/m^3)						
TEST 15	T=1.3[b]	T=12.3	T=24.3	T=48.3	T=96.3	T=120	T=168
Formaldehyde	25	31	NC[c]	38	19	19	14
Acetaldehyde	439	132	45	23	9.0	7.4	6.5
Propionaldehyde	2.1	ND[d]	ND	ND	ND	ND	ND
Benzaldehyde	23	6.5	5.1	2.7	ND	1.8	1.5
TEST 16	T=1.3	T=12.3	T=24.3	T=48.3	T=96.3	T=120	T=168
Formaldehyde	28	35	31	33	26	23	16
Acetaldehyde	431	129	46	22	10	8.6	7.4
Propionaldehyde	ND	ND	ND	ND	ND	ND	ND
Benzaldehyde	21	2.9	2.7	ND	ND	ND	ND
%RSD							
Formaldehyde	8.7	8.5	-	10	21	14	10
Acetaldehyde	1.2	1.9	0.6	3.4	8.1	11.1	9.1
Propionaldehyde	-	-	-	-	-	-	-
Benzaldehyde	7.3	54	44	-	-	-	-

[a]Tests 15 and 16 on Table 8-1, performed using Sherwin Williams 1604 Gloss: (Rose Dawn); Test 15 sample wt (10.79 g); Test 16 - sample wt (10.48 g).
[b]Sampling time in hours.
[c]Interference prevented quantitation.
[d]Below the method quantitation limit - see Table 8-13.

TABLE 8-36. RESULTS OF SINGLE CHAMBER REPEATABILITY TESTS (TESTS 17 AND 18) FOR ALDEHYDE EMISSIONS FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentration (μg/m³)						
TEST 17	T=1.3[b]	T=12.7	T=24.3	T=48.3	T=96.3	T=120	T=168
Formaldehyde	SL[c]	22	15	8.1	3.5	ND[d]	ND
Acetaldehyde	SL	17	8.8	4.1	ND	ND	ND
Propionaldehyde	SL	ND	ND	ND	ND	ND	ND
Benzaldehyde	SL	3.2	ND	ND	ND	ND	ND
TEST 18	T=1.3	T=12.7	T=24.3	T=48.3	T=96.3	T=120	T=168
Formaldehyde	36	25	17	8.5	3.5	ND	ND
Acetaldehyde	127	20	11	4.0	ND	ND	ND
Propionaldehyde	ND	ND	ND	ND	ND	ND	ND
Benzaldehyde	63	3.5	ND	ND	ND	ND	ND
%RSD							
Formaldehyde	-	10	6.6	3.4	0.0	-	-
Acetaldehyde	-	10	12	1.7	-	-	-
Propionaldehyde	-	-	-	-	-	-	-
Benzaldehyde	-	6.3	-	-	-	-	-

[a]Tests 17 and 18 on Table 8-1, performed using Glidden-64984 Semigloss: (Down Yonder) Test 17 sample wt (7.12 g); Test 18 sample wt (8.29 g).
[b]Sampling time in hours.
[c]Sample lost.
[d]Below the method quantitation limit - see Table 8-13.

formaldehyde and acetaldehyde. Highest concentrations in all tests were found for acetaldehyde at the earliest time points. Low concentrations of benzaldehyde were also measured in samples collected at the early time points during all the emissions tests. Propionaldehyde was not detected in any of the air samples. For both the single chamber repeatability and the interchamber variability test, reproducibility of measured air concentrations was generally acceptable (<30% RSD).

Table 8-37 provides results for Tests 19 and 20 which were designed to evaluate the effect of air surface velocities on emissions from paint samples. Results are presented as chamber air concentrations at each sampling point. Comparison of the air concentration data between the two tests, shows lower air concentrations for formaldehyde and acetaldehyde when the fan is used to mix the chamber air. This result shows the opposite trend that was found for VOC and SVOC emissions where higher air concentrations were found at the earlier time points when the fan was used.

Data for aldehyde emissions from the interchamber variability tests (Tests 11 and 12, Tests 13 and 14) for the alkyd paints are provided in Tables 8-38 and 8-39. Each table gives measured chamber air concentrations for samples collected at each time point for the paired tests. The variability of the measured concentrations between tests is presented as the %RSD for air samples collected at the same time point for each of the paired tests. Results of both set of tests show measurable emissions for formaldehyde and acetaldehyde although at lower levels than reported from the latex paints. Highest concentrations in all cases are found for acetaldehyde at the earliest time points. Low concentrations of propionaldehyde were also measured during emissions testing with the Glidden semigloss paint (Sea Foam). Benzaldehyde was not detected during emissions testing for the alkyd paints. For Test 13 and 14 (Table 8-39), reproducibility of measured air concentrations was generally acceptable (<30% RSD). In contrast, reproducibility for measured air concentrations between tests 11 and 12 (Table 8-39) was poor; highest %RSD values were calculated for acetaldehyde. The reason for the poor reproducibility is unknown and is not consistent with data generated for VOC air concentrations for the same tests.

8.3.6 Emission Parameters

Emission parameters for VOCs, SVOCs, and aldehydes in paint samples were estimated by fitting the chamber air concentration data from emissions testing to specific source models. For the aldehydes, emission parameters were generated only for

TABLE 8-37. RESULTS OF THE EFFECTS OF AIR VELOCITY ON THE EMISSIONS OF ALDEHYDES FROM LATEX PAINT[a] - CHAMBER AIR CONCENTRATIONS

Compound	Chamber Air Concentration (µg/m³)						
TEST 19 (FAN)	T=1.3[b]	T=12.3	T=24.3	T=48.3	T=96.3	T=120	T=168
Formaldehyde	25	14	5.7	SL[c]	6.8	3.3	ND[d]
Acetaldehyde	140	14	14	SL	NC[e]	NC	NC
Acrolein	ND	ND	ND	SL	ND	ND	ND
Propionaldehyde	ND	ND	ND	SL	ND	ND	ND
Benzaldehyde	14	6.3	0.90	SL	ND	ND	ND
TEST 20 (NO FAN)	T=1.3	T=12.3	T=24.3	T=48.3	T=96.3	T=120	T=168
Formaldehyde	29	25	3.7	2.9	2.7	ND	ND
Acetaldehyde	300	17	13	NC	NC	NC	NC
Acrolein	ND	ND	ND	ND	ND	ND	ND
Propionaldehyde	ND	ND	ND	ND	ND	ND	ND
Benzaldehyde	18	3.2	ND	ND	ND	ND	ND

[a]Tests 19 and 20 on Table 8-1, performed using Sherwin Williams 1629 Flat (Marmalade); Test 19 - sample wt (9.13 g); Test 20 - sample wt (10.6 g).
[b]Sampling time in hours.
[c]Sample lost.
[d]Below the method quantitation limit - see Table 8-13.
[e]Interference prevented quantitation.

TABLE 8-38. RESULTS OF INTERCHAMBER VARIABILITY TESTS (TESTS 11 AND 12) FOR ALDEHYDE EMISSIONS FROM ALKYD PAINT[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentration (μg/m³)							
TEST 11	T=0.63[b]	T=1.1	T=2.1	T=3.1	T=4.1	T=8.7	T=12.7	T=24.7
Formaldehyde	12.6	8.3	5.8	3.9	2.9	ND[c]	ND	ND
Acetaldehyde	22.1	11.8	7.6	7.1	4.4	5.0	7.8	5.7
Propionaldehyde	ND	ND	ND	ND	ND	ND	ND	4.1
Benzaldehyde	ND	ND	ND	ND	ND	ND	ND	ND
TEST 12	T=0.65	T=1.2	T=2.2	T=3.2	T=4.2	T=8.7	T=12.7	T=24.7
Formaldehyde	19.6	11.7	8.4	7.3	5.1	7.3	8.1	4.6
Acetaldehyde	53.4	26.4	23.8	28.5	20.6	39.3	45.7	25.1
Propionaldehyde	ND	ND	ND	ND	ND	ND	ND	ND
Benzaldehyde	ND	ND	ND	ND	ND	ND	ND	ND
%RSD								
Formaldehyde	31	24	26	43	39	-	-	-
Acetaldehyde	59	54	73	85	92	109	110	55
Propionaldehyde	-	-	-	-	-	-	-	-
Benzaldehyde	-	-	-	-	-	-	-	-

[a]Tests 11 and 12 on Table 8-1, performed using Glidden 5700-25312 Flat: (Chim Cham); Test 11 sample wt (13.53 g); Test 12 - sample wt (14.83 g).
[b]Sampling time in hours.
[c]Below the method quantitation limit - see Table 8-13.

TABLE 8-39. RESULTS OF INTERCHAMBER VARIABILITY TESTS (TESTS 13 AND 14) FOR ALDEHYDE EMISSIONS FROM ALKYD PAINT[a] - CHAMBER AIR CONCENTRATION

Compound	Chamber Air Concentration (μg/m^3)							
TEST 13	T=.65[b]	T=1.2	T=2.2	T=3.2	T=4.2	T=8.7	T=12.7	T=24.7
Formaldehyde	4.7	ND[c]	ND	SL[d]	ND	ND	ND	5.0
Acetaldehyde	19.3	11.4	6.9	SL	3.9	4.3	ND	8.4
Propionaldehyde	7.8	5.1	5.2	SL	2.1	1.7	1.8	6.9
Benzaldehyde	ND	ND	ND	SL	3.1	2.3	2.9	ND
TEST 14	T=.65[b]	T=1.2	T=2.2	T=3.2	T=4.2	T=8.7	T=12.7	T=24.7
Formaldehyde	6.2	ND	ND	ND	ND	3.4	ND	3.2
Acetaldehyde	21.9	13.7	10.3	9.8	4.4	5.6	ND	6.1
Propionaldehyde	8.1	4.4	3.8	3.3	2.1	1.6	1.9	NC
Benzaldehyde	ND	ND	ND	ND	ND	ND	ND	ND
%RSD								
Formaldehyde	19	-	-	-	-	-	-	31
Acetaldehyde	8.9	13	28	-	8.5	18	-	22
Propionaldehyde	2.7	10	22	-	0	4.3	3.8	-
Benzaldehyde	-	-	-	-	-	-	-	-

[a]Tests 13 and 14 on Table 8-1, performed using Glidden 8000-46212 Semigloss; (Sea Foam); Test 13 - sample wt (11.19 g); Test 14 - sample wt (12.23 g).
[b]Sampling time in hours.
[c]Below the method quantitation limit - see Table 8-13.
[d]Sample lost.

formaldehyde and acetaldehyde emissions from latex paints. Two models were used, as determined by the character of the data. The first is a simple, exponentially decaying source:

$$S(t) = S_0 e^{-kt} \tag{8-10}$$

where

t is time after placing the paint sample in the chamber, h;
S(t) is the source strength at time t, mg/h·g of paint;
S_0 is the initial source strength, mg/h·g of paint; and
k is the decay constant, h^{-1}.

This model can be combined with a well-mixed chamber model to predict the concentration in the chamber as a function of time:

$$C(t) = \frac{LS_0(e^{-kt} - e^{-Nt})}{N - k} \tag{8-11}$$

where

C(t) is the analyte concentration at time t, mg/m^3;
N is the air change rate, h^{-1};
L is the product loading, g/m^3; and
all other terms are as before.

This model works well for some paints but not for others. The data indicate that the chamber concentration at time t = 0 may not be zero, but instead may be almost equal to the peak concentration measured. This may happen if paint emissions are carried into the chamber as the plate is inserted. In such cases, a three-parameter fit to the data is made, using:

$$C(t) = \frac{LS_0(e^{-kt} - e^{-Nt})}{N - k} + C_0 e^{-Nt} \tag{8-12}$$

where

C_0 is a fitting parameter representing concentration in the chamber at time t = 0, mg/m^3 .

In fact, this equation was used in preference to Equation 8-11 to allow the fitting procedure to evaluate the initial chamber concentration, whether or not it appears to be zero.

The latex paints contained some components that were well-described by this equation, but others showed a maximum concentration at times as long as 50 hours after application. Fitting this data requires a source whose strength builds up with time, as if there is a slow diffusion of the components to the surface of the paint, from where it is volatilized.

The concentration equation used for this case is:

$$C(t) = \frac{LS_0(1 - e^{-k_2 t})(e^{-kt} - e^{-Nt})}{N - k} \tag{8-13}$$

where

k_2 presents a time constant for emission buildup, h^{-1}.

This corresponds approximately to a source model given by:

$$S(t) = S_0 e^{-kt}(1 - e^{-k_2 t}) \tag{8-14}$$

The model fitting criterion was the minimization of the quantity R:

$$R = \sum_1^n \frac{(C(t) - C_{exp}(t))^2}{C_{exp}(t)} \tag{8-15}$$

where

C(t) is the predicted concentration at time t, mg / m^3;

C_{exp}(t) is the measured concentration at time t; and

n is the number of data points in the set being fitted.

The denominator in Equation 8-15 is chosen for the following reason. If the power of C_{exp} is 0 (or C_{exp} is removed from the denominator), the concentrations of highest magnitude, near time t = 0, determine the fitting parameters; if the power of C_{exp} is 2, then all concentrations affect the fitting parameters equally, especially those of lower precision at the lowest concentration. Using the power 1 for C_{exp} gives the higher concentration data more weight, but does not completely eliminate the influence of the lower concentration measurements.

The overall goodness of fit is described by the relative standard deviation of the fit (STD), given by:

$$STD = 100 \frac{\sqrt{\frac{R}{n - 1}}}{MAX(C_{exp})} \tag{8-16}$$

where

R is defined by Equation 8-15; and

$MAX(C_{exp})$ is the maximum concentration measured for the analyte under consideration.

STD is not strictly an accurate standard deviation because it does not take into account the data weighting in Equation 8-15, nor the number of fitting parameters. It is adequate for ranking the fits and setting a cutoff value for which the fit does not represent the data very well.

For the chamber test here, STD values less than 0.10 were considered good and values between 10 and 20 were considered acceptable. Values above 0.20 indicate that the model does not give a very good fit to the measured concentrations; however, the poor fit is often only at one or two times out of six or more. Moreover, the fits to the aldehyde data give high STD primarily because the maximum concentrations are much lower than the other analyte concentrations.

The fitted models can be integrated analytically over time to compute the total emission from the paint for each analyte. For those analytes with nonzero concentrations at time t = 0, the mass of vapor in the chamber is also included in the emissions for that analyte. In general, the computed emissions agree well with the analyses of the analyte fractions in the bulk paint, as discussed below.

Estimated emission parameters (S_o, k_1, k_2, and STD) are given in Table 8-40 for alkyd paints and in Table 8-41 for the latex paints. Appendix D gives all of the calculated emission data plots of the theoretical and measured chamber air concentrations plotted over time for all target analytes and emission tests.

When estimating emission parameters, results from paired chamber tests were combined (i.e., single chamber repeatability and interchamber variability tests for each paint). A review of the plots in Appendix D shows that in most cases, the differences in measured air concentration for paired chamber tests were smaller than the differences between the measured and theoretical air concentration. When test results are combined, the STD reflects both the variability between air concentrations measured in paired tests and between the measured and the theoretical air concentrations.

The results in Table 8-40 and 8-41 and the plots in Appendix D show that the decaying source model, Equation 8-10, represents most of the components in both types of paint quite well. The slow buildup model, Equation 8-13, does not fit the latex paint analytes as well as the decaying source model fits the alkyd analytes, but it does capture the general pattern of the latex emissions. As a result, it appears that the alkyd paints produce their peak concentration about 5 hours after application, but the latex paints do not peak until about 50 hours after application.

For a few analytes, particularly n-dodecane and pentylcyclohexane, the concentrations appear to peak at times well beyond five hours, but there are not enough long time data to define the parameters of the slow buildup model. For these components, the present models do not define the concentration behavior very well, even though the STDs are not extreme.

In addition, many of the alkyd analytes do not agree very well with the model fits at 24 hours after application. Most of the measured 24 hour concentrations are much higher than the model predicts. This indicates that there is a slow decay process in addition to the rather rapidly decaying source determined by the fit. The impact of the slowly decaying source on the total emissions is small, but not completely negligible.

Although the presence of a slowly decaying source can be modeled for the alkyd paints, the present data would not define the parameters adequately. Concentrations measurement would be needed at 16, 30, 36, 42, and 48 hours after application to provide

TABLE 8-40. EMISSION PARAMETERS[a] CALCULATED FROM SMALL CHAMBER EMISSIONS TESTS FOR ALKYD PAINTS

	GL[b]-Gloss (Hyacinth) Tests 5 and 6			GL - Flat (Chim Cham) Tests 11 and 12			GL[a] - Semigloss (Sea Foam) Tests 13 and 14			SW[c] - Gloss (Bumbershoot)					
										Test 21[d]			Test 22[e]		
Compounds	S_o	k	STD	S_o	k	STD	S_o	k	STD	S_o	k	STD	S_o	k	STD
m,p-Xylene	1.1	.55	.059	.26	.46	.026	.086	.42	.022	1.1	.69	.006	1.2	.48	.007
n-Nonane	3.2	.46	.033	.12	.27	.084	1.0	.28	.024	5.2	.62	.005	3.0	.31	.004
o-Xylene	.34	.47	.096	.057	.38	.045	.23	.34	.033	.26	.66	.028	.19	.39	.018
Propylcyclohexane	1.1	.44	.064	.031	.25	.19	.26	.27	.057	1.4	.58	.010	.79	.28	.010
3- & 4-Ethyl toluene	.55	.28	.050	.024	.20	.15	.20	.17	.047	.091	.40	.042	.050	.18	.033
1,3,5-Trimethylbenzene	.19	.23	.076	.009	.18	.35	.064	.14	.095	.058	.38	.070	.022	.14	.063
n-Decane	4.8	.23	.020	.40	.15	.062	1.2	.23	.050	7.8	.33	.011	3.2	.17	.018
2-Ethyl toluene	.18	.35	.15	.008	.17	.30	.068	.18	.14	.026	.34	.082	.012	.14	.034
1,2,4-Trimethylbenzene	.58	.22	.043	.027	.16	.19	.18	.12	.064	.14	.31	.038	.070	.16	.12
1,2,3-Trimethylbenzene	.15	.16	.080	.008	.13	.34	.050	.083	.097	.035	.25	.059	.015	.12	.27
2-Methyldecane	.26	.14	.082	.17	.13	.14	.11	.050	.12	.80	.20	.047	.21	.047	.090
trans-Decahydronaphthalene	.43	.18	.058	.25	.13	.079	.17	.073	.068	.99	.26	.019	.36	.11	.058
n-Undecane	.80	.076	.045	1.0	.23	.061	.74	.21	.077	3.6	.19	.019	.84	.03	.029
Pentylcyclohexane	.055	.046	.26	.11	.11	.16	.049	.026	.10	.26	.13	.13	.61	-.01	.084
n-Dodecane	.069	-.02	.11	.12	.039	.13	.070	.002	.087	.41	0.042	.075	.08	-.06	.006
TVOC	60	.22	.005	10	.070	.014	13	.096	.011	67	0.21	.001	29	.098	.003

[a] S_o = initial source strength (mg/h · g of paint).
k = decay rate (h^{-1}).
STD = % Relative standard deviation of fix.

[b] Glidden.

[c] Sherwin Williams.

[d] Test with fan.

[e] Test without fan.

TABLE 8-41. EMISSION PARAMETERS[a] CALCULATED FROM SMALL CHAMBER EMISSIONS TESTS FOR LATEX PAINTS

	SW[b] Flat (Marmalade)	SW-Gloss (Rose Dawn)	GL[c]-Semi-Gloss (Down Yonder)	SW-Flat (Marmalade)	
Compound	Tests 3 and 4	Tests 15 and 16	Tests 17 and 18	Test 19[d]	Test 20[e]
1,2-Propanediol					
S_o	0.51	0.51	80	3.3	2.1
k_1	0.023	0.023	0.048	0.054	0.036
k_2	0.003	0.0030	0.0024	0.0016	0.0015
STD	0.27	—	0.03	0.15	0.126
Ethylene glycol					
S_o	5.8	10.3	45	40	24
k_1	0.014	0.018	0.031	0.035	0.023
k_2	0.0014	0.0020	0.0009	0.0008	0.0007
STD	0.11	0.045	0.041	0.069	.069
2(2-Butoxyethoxy)ethanol					
S_o	0.40	4.1	2.9	0.020	0.013
k_1	0.024	0.022	0.024	0.017	0.010
k_2	0.0019	0.0033	0.0023	0.035	0.23
STD	0.37	0.094	0.21	0.095	0.061
Texanol					
S_o	0.066	0.012	0.137	0.079	0.054
k_1	0.0081	0.0062	0.0050	0.013	0.008
k_2	191	0.10	5.9	1.9	1.4
STD	0.12	0.30	0.068	.033	0.035
Formaldehyde					
S_o	$5.1E^{-5}$	$1.8E^{-4}$	$2.0E^{-4}$	$3.9E^{-5}$	$1.9E^{-5}$
k_1	$1.0E^{-2}$	$5.6E^{-3}$	.025	$3.9E^{-3}$	$4.1E^{-3}$
k_2	$1.4E^{-2}$	0	.0058	$8.0E^{-3}$	$8.5E^{-3}$
STD	0.95	2.12	0.080	1.9	0.360
Acetaldehyde					
S_o	$1.0E^{-4}$	$8.6E^{-4}$	$2.0E^{-4}$	$8.2E^{-5}$	$1.1E^{-4}$
k_1	$1.1E^{-2}$	$4.4E^{-2}$	$4.4E^{-2}$	$5.0E^{-4}$	$2.5E^{-2}$
k_2	$1.1E^{-1}$	$1.0E^{-1}$	$4.4E^{-2}$	$4.9E^{-2}$	$9.5E^{-2}$
STD	0.368	0.466	0.17	0.001	>0.000
TVOC					
S_o	20	30	305	0.82	0.51
k_1	0.019	0.020	.042	0.021	0.011
k_2	0.0009	0.0012	.00084	0.12	0.095
STD	0.069	0.033	0.023	.026	0.046

[a] S_o = initial source strength (mg/h · g of paint).
k_1 = decay rate (h^{-1}), k_2 = time constant for emission buildup (h^{-1}).
STD = Standard Deviation of fit.
[b] Sherwin Williams.
[c] Glidden.
[d] Test with fan.
[e] Test without fan.

enough experimental data for good parameter determination. Although the concentrations for these compounds were relatively low, chamber air concentrations at these later time points may fall below the method quantitation limit.

Table 8-42 gives the estimated mass of each VOC and TVOC emitted per gram of paint during the small chamber tests. These masses were estimated as the area under the theoretical concentration as time curve from t = o to t = infinity. Table 8-43 also gives the mass of each VOC and TVOC per gram of paint measured during bulk product analysis of the same paint samples. The difference between the estimated mass emitted and the mass measured in the bulk paint samples is presented as the % RSD calculated for the two measures. For TVOC, the mass per gram of paint estimated from the ASTM methods is also given. Similar data are given for the latex paints in Table 8-43. Results generally show good agreement between the two measures suggesting that the emissions data and modeling parameters are describing the paint emissions adequately.

TABLE 8-42. COMPARISON OF DATA FOR CHAMBER EMISSIONS TESTS TO RESULTS FOR BULK PRODUCT ANALYSIS FOR ALKYD PAINTS

	GL[a]-Gloss (Hyacinth) Tests 5 and 6			GL - Flat (Chim Cham) Tests 11 and 12			GL - Semigloss (Sea Foam) Tests 13 and 14			SW[b] - Gloss (Bumbershoot)					
										Test 21			Test 22		
Compounds	Me[c] (mg/g)	C_b[d] (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD
m,p-Xylene	2.3	3.6	31	1.3	1.6	13	2.7	4.0	27	3.4	4.3	16	3.1	4.3	23
n-Nonane	6.9	9.8	25	0.90	0.68	20	4.6	5.3	10	13	11	9	11	11.2	2.6
o-Xylene	0.76	1.1	26	0.41	0.37	8	0.98	1.1	7	0.65	0.83	17	0.65	0.83	17
Propylcyclohexane	2.6	4.2	33	0.26	0.20	18	1.1	1.5	19	3.0	3.4	9	3.0	3.4	9
3- & 4-Ethyl toluene	1.9	1.8	3.8	0.26	ND[e]	–	1.5	1.3	10	0.39	ND	–	0.34	ND	–
1,3,5-Trimethylbenzene	0.82	0.79	2.8	0.10	ND	–	0.61	0.52	11	0.15	ND	–	0.18	ND	–
n-Decane	21	18	11	5.0	4.5	7	5.9	14	58	25	19	18	20	19	2.5
2-Ethyl toluene	0.51	0.62	13	0.090	ND	–	0.42	0.48	10	0.13	ND	–	0.12	ND	–
1,2,4-Trimethylbenzene	2.6	2.8	4.2	0.31	ND	–	2.0	1.8	7	0.46	0.53	10	0.44	0.53	14
1,2,3-Trimethylbenzene	0.9	0.84	7	0.12	ND	–	0.81	0.64	17.1	0.19	ND	–	0.13	ND	–
2-Methyldecane	1.9	2.0	3.7	2.2	3.2	2.7	3.3	2.6	16	3.9	3.2	13.1	4.3	3.2	21
trans-Decahydronaphthalene	2.4	2.1	8.5	3.5	3.2	5	3.1	2.6	13	4.2	3.5	13.7	3.3	3.5	4.0
n-Undecane	10	9.1	7.3	5.5	19	78	3.6	16	91	19	16	10	28	16	38
Pentylcyclohexane	1.2	0.52	56	1.7	3.0	39	2.7	2.1	19	2.0	2.2	5.4	>1.5	2.2	–
n-Dodecane	>1.7	2.6	–	5.9	12	46	>1.7	8.1	–	9.7	7.9	15	>1.9	7.9	–
TVOC	280	280	0	310	180	38	220	210	3.2	560	270	49	430	270	32
		380[e]	21		299[e]	56		330[e]	28		540[e]	2.6		540[e]	16

[a] Glidden.
[b] Sherwin Williams.
[c] Estimated mass per gram of paint during chamber tests.
[d] Measured concentration measured during bulk product analysis.
[e]. Below the method quantitation limit.
[f] Estimated concentration from ASTM methods.

TABLE 8-43. COMPARISON OF DATA FOR CHAMBER EMISSIONS TESTS TO RESULTS FOR BULK PRODUCT ANALYSIS FOR LATEX PAINTS

	SW[a]-Flat (Marmalade) Tests 3 and 4			SW - Gloss (Rose Dawn) Tests 15 and 16			GL[b] - Semigloss Sand Yonder ~~(Sea Foam)~~ Tests 17 and 18			SW - Flat (Marmalade) Test 19			SW - Flat (Marmalade) Test 20		
Compounds	Me[c] (mg/g)	C_b[d] (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD	Me (mg/g)	C_b (mg/g)	%RSD
1,2-Propanediol	2.6	ND	–	NC	ND	–	79	38	49	1.9	ND	–	2.1	ND	–
Ethylene glycol	37	29	17	60	48	15	45	19	57	25	29	10	30	29	2
2-(2-Butoxyethoxy)ethanol	1.2	1.5	18	25	13	46	11	4.4	60	1.1	1.5	24	1.3	1.5	12
Texanol	14	5.1	66	2.7	~~27~~ 2.7	1	89	5.7	124	14	5.1	66	16	5.1	73
TVOC	49	36	22	88	65	21	140	68	49	34	36	3	41	36	10
		65[e]	20		84[e]	3		93[e]	31		65[e]	44		65[e]	32
Formaldehyde	0.08	NM[f]	–	0.03	NM	–	0.02	NM	–	0.12	NM	–	0.11	NM	–
Acetaldehyde	0.53	NM	–	0.14	NM	–	0.06	NM	–	NC[g]	NM	–	0.21	NM	–

[a] Sherwin Williams.
[b] Glidden.
[c] Estimated mass emitted per gram of paint during chamber tests.
[d] Concentration measured during bulk product analysis.
[e] Estimated concentration from ASTM methods (Table 6-1).
[f] Not measured.
[g] Not calculated - curve did not adequately describe the data.

SECTION 9.0
METALS ANALYSIS

9.1 STUDY DESIGN

Two methods were evaluated for the analysis of metals in alkyd and latex paints. The target list of metals provided by EPA is given in Table 9-1. The first method used X-ray fluorescence spectroscopy (XRF) on untreated liquid paint samples. The second method used inductively coupled plasma emission spectroscopy (ICP) on digested paint samples. The XRF method was performed on single aliquots of each of the 20 paint samples shown in Table 9-2 to provide data on metal concentrations in each sample. The ICP method was performed on triplicate aliquots (from the same vials) for each of the 20 paint samples to provide data on metal concentrations and method precision. For the ICP method, additional QC samples including method blanks (unspiked reagents), method controls (spiked reagents), and matrix spikes (spiked paint samples) were prepared, digested, and analyzed to provide additional information on method performance.

9.2 METHOD

9.2.1 ICP Method

9.2.1.1 Sample Preparation

Homogenized paint samples (0.25 g) were placed in an acid washed Teflon digestion vessel (CEM Corp, Mathews, NC). Concentrated nitric acid (15 mL) (Baker Instranalyzed) and 2 mL of AES hydrofluoric acid (Baker Instranalyzed) were added. The vessels were capped according to the manufacturers directions and placed in a CEM MDS810 microwave digestion system and heated according to the following program:

- 10 minutes at 600 Watts (100% power)
- 8 minutes at 480 watts
- 10 minutes at 600 watts

All 12 positions in the MDS81D sample carousel were filled with sample vessels containing an equivalent volume of sample mixture or water in order to distribute the microwave energy evenly.

After the heating program was completed, the sample vessels were allowed to cool to room temperature. The digestion residues were then dissolved by adding 50 mL of

TABLE 9-1. TARGET METALS FOR LIQUID PAINTS BY XRF AND ICP

Aluminum	Manganese	Tin
Chromium	Cobalt	Barium
Molybdenum	Nickel	Mercury
Cadmium	Copper	Arsenic
Antimony	Selenium	
Lead	Strontium	

TABLE 9-2. PAINT SAMPLES FOR METAL ANALYSIS

Paint Type	Gloss Type	Manufacturer Series	Color Group	Manufacturer's ID No.	Color Name
SHERWIN WILLIAMS					
(1) Alkyd	Flat	ProMar 200	Yellow	SW1352	Crescent Cream
(2) Alkyd	Semi-gloss	ProMar 200	Blue	SW1529	Violet Veil
(3) Alkyd	Gloss	ProMar 200	Green	SW1435	Bumbershoot
(4) Latex	Flat	ProMar 200	Orange	SW1629	Marmalade
(5) Latex	Semi-gloss	ProMar 200	Purple	SW1545	Vibrant Violet
(6) Latex	Gloss	ProMar 200	Red	SW1604	Rose Dawn
(7) Latex	Flat	ProMar 200	Green	SW1734	Grass Roots
(8) Latex	Semi-gloss	ProMar 200	Other	SW1125	Praline
(9) Alkyd	Flat	ProMar 200	Other	SW1003	First Star
(10) Alkyd	Semi-gloss	ProMar 200	Other	SW1309	Coral Canyon
GLIDDEN					
(1) Alkyd	Flat	5700	Yellow	25312	Chim Cham
(2) Alkyd	Semi-gloss	UH8000	Green	46212	Seafoam
(3) Alkyd	Gloss	4550	Purple	76262	Hyacinth
(4) Latex	Flat	3480	Red	01044	Tomahawk
(5) Latex	Semi-gloss	UH6380	Blue	64984	Down Yonder
(6) Latex	Gloss	6918	Orange	16112	Orange Glaze
(7) Latex	Semi-gloss	UH6300	Blue	64542	Ice Cap
(8) Latex	Gloss	6987	Orange	20573	Orange Ice
(9) Alkyd	Flat	5718	Green	34722	Antigua
(10) Alkyd	Gloss	4550	Other	20852	Sheriff's Star

laboratory pure water (ASTM Type II) and the vessels recapped and microwaved for an additional 20 minutes at 300 watts (50% power). The resulting digest was then transferred to a 100 mL volumetric flask and diluted to volume with laboratory pure water. Matrix spikes, method blanks and method controls were similarly prepared, each at a 5% frequency.

9.2.1.2 Sample Measurement

The aqueous digests were analyzed using a Leeman Labs (Lowell, MA) Plasmaspec I sequential inductively coupled plasma emission spectrometer (ICP). Calibration is performed quarterly using a four or five point calibration curve. Calibration updates are performed using a blank and a mid level standard every 7-10 samples. The accuracy of the calibration/update standards is verified daily through the analysis of calibration check standards prepared or purchased from a different source than those of the calibration/update standards. This analysis should be within 5% of the expected value or the calibration is repeated. Update sample analyses should be within 10% of expected value or samples analyzed since the last successful update are reanalyzed.

9.2.2 XRF Analyses

XRF screening of paint samples was performed by Dr. T. M. Spittler of EPA Region 2. A description of the method used is provided in Appendix E.

9.3 RESULTS

Results for the analysis of paint samples by both ICP and XRF method are summarized for the alkyd paints in Table 9-3 and for the latex paints in Table 9-4. Each table provides information on measured concentrations of target metals in paint samples. For the ICP method where triplicate aliquots were measured, concentration data are provided as the mean and the %RSD of the triplicate determinations. For the XRF method, only a single aliquot was analyzed for each paint. Several additional elements were analyzed by the XRF method. For the paint samples analyzed by ICP, results with high variability (%RSD > 30) are also highlighted on the tables. Generally, precision of the ICP test method was acceptable. For some samples the measured %RSD values for all metals with measurable concentrations were high (>30%). It is suspected that this was a result of using sample aliquots that were poorly mixed. In other samples, unacceptable precision was

TABLE 9-3. RESULTS OF METALS ANALYSIS FOF ALKYD PAINTS

	Mean Measured Concentration in µg/g (%RSD)[a]									
	Flat Crescent Green		Flat First Star		Semigloss Coral Canyon		Semigloss Violet Veil		Gloss Bumbershoot	
Metal	ICP[b]	XRF[c]	ICP	XRF[a]	ICP	XRF	ICP	XRF	ICP	XRF
SHERWIN WILLIAMS										
Aluminum	33,000(53)	NA[d]	25,000(9.0)	NA	4,200(9.0)	NA	4,000(9.0)	NA	5,500(19)	NA
Selenium	<60[e]	<2	<60	<2	<60	<2	<60	<2	113*	<2
Barium	17**(53)	<50	11(14)	<50	0.68*	<50	0.7*	<50	2.5 (57)	<50
Antimony	<40	<5	<40	<5	<40	<5	55	<5	59(19)	<5
Cobalt	190(59)	<20	160**(10)	<20	97**(82)	<20	160(12)	<20	170(15)	<20
Cadmium	<1.0	<5	<1.0	<5	<1.0	<5	<1.0	<5	<1.0	<5
Arsenic	39(13)	<20	<30	<20	37*	<20	<30	<20	<30	<20
Chromium	26**(59)	10	18**(14)	<5	8.3(28)	<5	4.9(6.4)	<5	4.7(24)	<5
Copper	<2.0	6	<2.0	9	31*	9	<2.0	10	<2.0	24
Strontium	220**(58)	NA	140**(12)	NA	36**(39)	NA	45(12)	NA	5.4(75)	NA
Lead	35*	10	26*	<10	18**(6.7)	30	21(22)	33	<15	<10
Manganese	14**(52)	<5	37(25)	15	6.5(4.2)	<5	8.8(29)	<5	3.9(24)	<5
Molybdenum	<5.0	<5	<5.0	<5	<15	<5	<5.0	<5	<5.0	<5
Nickel	50*	7	<15	10	64*	5	<15	5	<15	<15
Mercury	86(52)	<10	76**(3.8)	<10	53**(39)	<10	83(44)	<10	62(42)	<10
Tin	119*	<25	<75	<25	<75	<25	<75	<25	112*	<25
Zinc	NA	9	NA	6	NA	6	NA	5	NA	<1
Bismuth	NA	<5	NA	<5	NA	<5	NA	<5	NA	<5
Calcium	NA	10.5%	NA	10.5%	NA	5.0%	NA	4.6%	NA	<0.1%
Titanium	NA	14.0%	NA	14.6%	NA	29.8%	NA	28.5%	NA	40.0%
Iron	NA	2500	NA	540	NA	3800	NA	470	NA	500

TABLE 9-3. RESULTS OF METALS ANALYSIS FOR ALKYD PAINTS (CONTINUED)

	Mean Measured Concentration in μg/g (%RSD)[a]									
	Flat Tomahawk		Semigloss Down Yonder		Semigloss Ice Cap		Gloss Orange Glaze		Gloss Orange Ice	
Metal	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF
GLIDDEN										
Aluminum	11,000(26)	NA	25,000(9)	NA	13,000(15)	NA	1600(43)	NA	3600(30)	NA
Selenium	<60	<2	<60	<2	<60	<2	70*	<2	<60	<2
Barium	13(27)	<50	14(11)	<50	7.3(22)	<50	<0.5	<50	14(35)	<50
Antimony	<40	<5	<40	<5	<40	<5	<40	<5	<40	<5
Cobalt	<10	<20	16(14)	<20	105(19)	<20	52(101)	<20	64(30)	<20
Cadmium	<1.0	<5	<1.0	<5	<1.0	<5	<1.0	<5	<1.0	<5
Arsenic	<30	<20	<30	<20	46**(14)	<20	<30	<20	33**(12)	<20
Chromium	7.3(25)	13	15(13)	7	4.3(8.3)	<5	4.6(39)	<5	4.9**(15)	<5
Copper	<2	7	170(7.2)	172	<2.0	34	<2.0	8	<2.0	7
Strontium	190(27)	NA	23(3.9)	NA	9.9(13)	NA	1.3**(22)	NA	2.7**(31)	NA
Lead	<15	<5	<15	9	<15	<10	<15	<10	<15	<10
Manganese	14(26)	<5	2.2(6.4)	<5	2.6(5.7)	<5	3.4(31)	<5	2.5**(2.3)	12
Molybdenum	<5	<5	<5.0	<5	<5.0	<5	<5.0	<5	<5	<5
Nickel	<15	4	<15	8	<15	5	<15	5	<15	5
Mercury	<30	<10	<30	10	33(9.2)	<10	<30	<10	31*	<10
Tin	<75	<25	<75	<25	<75	<25	<75	<25	<75	<25
Zinc	NA	4	NA	8	NA	4	NA	7	NA	5
Bismuth	NA	<5	NA	<5	NA	<5	NA	<5	NA	<5
Calcium	NA	5.4%	NA	<0.1%	NA	<0.1%	NA	<0.1%	NA	<0.1%
Titanium	NA	1.2%	NA	1.5%	NA	16.1%	NA	34.0%	NA	15.8
Iron	NA	6800	NA	640	NA	1060	NA	6840	NA	308

FOOTNOTES:

[a] Numbers with squares around them indicate where RSD of ICP analysis was greater than 30%.

* A value above the QL was found in only one of three replicate samples; % RSD value was not calculated.

** Values above the QL were found in two of the three replicate samples. Mean and % RSD calculated for only samples above the QL.

[b] Triplicate sample analyzed.

[c] Only single replicate analyzed by XRF.

[d] Not analyzed by method.

[e] Less than the quantitation limit (QL) as indicated.

TABLE 9-4. RESULTS OF METALS ANALYSIS FOR LATEX PAINTS

	Mean Measured Concentration in µg/g (%RSD)[a]									
	Flat Marmalade		Flat Grass Root		Semigloss Vibrant Violet		Semigloss Praline		Gloss Rose Dawn	
Metal	ICP[b]	XRF[c]	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF
SHERWIN WILLIAMS										
Aluminum	12,000(4)	NA[d]	13,000(15)	NA	4600(5)	NA	1500(35)	NA	3300(16)	NA
Selenium	<60[c]	<2	<60	<2	<60	<2	<60	<2	<60	<2
Barium	6.7(18)	<50	15(75)	<50	3.5(15)	<50	1.5(7.3)	<50	<0.5	<50
Antimony	<40	<5	<40	<5	<40	<5	<40	<5	<40	<5
Cobalt	51(13)	<20	55(14)	<20	55(3.2)	<20	50(22)	<20	140(19)	<20
Cadmium	<1.0	<5	<1.0	<5.0	<1.0	<5	<1.0	<5	<1.0	<5
Arsenic	<30	<20	<30	<20	<30	<20	<30	<20	<30	<20
Chromium	7.5(44)	9	10(14)	<5.0	<2.0	<5	3.4(16)	9	<2.0	<5
Copper	<2.0	5	570(17)	440	12(58)	49	<2.0	10	<2.0	7
Strontium	10(16)	NA	13(17)	NA	29(7.0)	NA	29(8.9)	NA	<1.0	NA
Lead	<15	<5	29[*]	<5	<15	12	<15	12	<15	<5
Manganese	5.4(10)	<5	7.4(28)	<5	3.2(26)	7	10(62)	<5	<2.0	<5
Molydenum	<5.0	<5	<5.0	<5	<5.0	<5	<5.0	<5	<5.0	<5
Nickel	<15	7	<15	<1	<15	7	<15	4	<15	10
Mercury	<30	<10	72(64)	<10	35(3.4)	<10	32[**](6.0)	<10	48(19)	<10
Tin	<75	<25	<75	<25	<75	<25	<75	<25	<75	<25
Zinc	NA	34	NA	<1	NA	69	NA	9	NA	48
Bismuth	NA	<5	NA	<5	NA	<5	NA	<5	NA	<5
Calcium	NA	<0.1%	NA	<0.1%	NA	1.9%	NA	2.0%	NA	<0.1%
Titanium	NA	10%	NA	6.8%	NA	9.6%	NA	10%	NA	27%
Iron	NA	760	NA	2300	NA	500	NA	6100	NA	240

TABLE 9-4. RESULTS OF METALS ANALYSIS FOR LATEX PAINTS (CONTINUED)

	Mean Measured Concentration in µg/g (%RSD)									
	Flat Antigua		Flat Chim Cham		Semigloss Sea Foam		Gloss Sheriff's Star		Gloss Hyacinth	
Metal	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF
GLIDDEN										
Aluminum	12,000(12)	NA	34,000(5)	NA	6,200(10)	NA	8,200(13)	NA	12,000(43)	NA
Selenium	<60	<2	<60	<2	<60	<2	<60	<2	<60	<2
Barium	30(5.8)	<50	20(16)	<50	1.4(36)	<50	1.7(29)	<50	7.3(40)	<50
Antimony	<40	<5	<40	<5	<40	<5	40*	<5	<40	<5
Cobalt	170(8.8)	<20	170(4.3)	<20	300(21)	<20	370(17)	<20	460(38)	125
Cadmium	<1.0	<5	<1.0	<5	<1.0	<5	<1.0	<5	<1.0	<5
Arsenic	47*	<20	52**(10)	<20	<30	<20	39*	<20	<30	<20
Chromium	11(12)	<5	24(7.2)	15	3.8(19)	<5	9.1(15)	<5	8.0(56)	<5
Copper	<2.0	15	<2.0	8	<2.0	5	<2.0	6	33(26)	66
Strontium	290(7.0)	NA	190(17)	NA	210(23)	NA	3.2(51)	NA	4.0(43)	NA
Lead	23*	12	30(55)	10	<15	<10	19*	30	<15	21
Manganese	18(7.9)	15	16(41)	12	<2.0	<5	8.5(114)	15	<2.0	<5
Molybdenum	<5.0	<5	<5.0	<5	20**(25)	<5	<5.0	<5	<5.0	<5
Nickel	<15	7	<15	7	<15	<1	<15	<1	<15	<1
Mercury	80(9.1)	<10	7.7(14)	<10	<30	<10	63(18)	<10	56**(52)	<10
Tin	147*	<25	<75	<25	<75	<25	<75	<25	<75	<25
Zinc	NA	8	NA	7	NA	2680	NA	5	NA	5
Bismuth	NA	<5	NA	<5	NA	<5	NA	10	NA	<5
Calcium	NA	15.5%	NA	10.0%	NA	8.7%	NA	<0.1%	NA	<0.1%
Titanium	NA	15.0%	NA	11.2%	NA	26.0%	NA	50.0%	NA	45.0%
Iron	NA	630	NA	1500	NA	950	NA	3050	NA	150

FOOTNOTES:

[a] Numbers with squares around them indicate where RSD of ICP analysis was greater than 30%.

* A value above the QL was found in only one of three replicate samples; % RSD value was not calculated.

** Values above the QL were found in two of the three replicate samples. Mean and % RSD calculated for only samples above the QL.

[b] Triplicate sample analyzed.

[c] Only single replicate analyzed by XRF.

[d] Not analyzed by method.

[e] Less than the quantitation limit (QL) as indicated.

seen for only a few of the metals. This is most likely due to problems associated with the digestion that did not adequately remove all samples prior to analysis interferences. A comparison between the results for analysis by the ICP and XRF methods shows that measured concentrations often differed by greater than a factor of two.

Table 9-5 summarizes information in Tables 9-3 and 9-4 and gives the percentage of samples with measurable concentration of metals. Percent measurable values are provided by manufacturer and paint type as well as for all paint samples.

Method performance results for the ICP method are provided in Table 9-6. Generally, method blanks were uncontaminated. Method controls showed acceptable recovery (>80%) and reproducibility (%RSD <15). Exceptions to this were strontium and molybdenum which give high %RSD values. Spiked paint samples generally showed good recovery. The single exception was a very low recovery for aluminum in one of the spiked samples. However, the analyses of the three unspiked samples of that paint gave very high and variable concentrations for aluminum. Under these conditions, it was felt that meaningful recovery data could not be determined.

TABLE 9-5. PERCENTAGE OF PAINT SAMPLES WITH MEASURABLE CONCENTRATIONS OF METALS

	Quantitative Limit (µg/g)		% Measurable									
			Latex				Alkyd					
			Sherwin Williams		Glidden		Sherwin Williams		Glidden		ALL	
	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF
Aluminum	50	—[a]	100	—[a]	100	—	100	—	100	—	100	—
Selenium	60	2	0	0	20	0	20	0	0	0	0	0
Barium	0.5	50	80	—	80	0	100	0	80	0	90	0
Antimony	40	5	0	0	20	0	40	0	0	0	15	0
Cobalt	10	20	100	0	100	20	100	0	80	0	95	5
Cadmium	1.0	5	0	0	0	0	0	0	0	0	0	0
Arsenic	30	20	0	0	60	0	40	0	40	0	35	0
Chromium	2.0	5	60	40	100	20	100	20	100	40	90	30
Copper	2.0	2	40	100	20	100	20	100	20	100	25	100
Strontium	1.0	—	80	—	100	—	100	—	100	—	95	—
Lead	15	10	20	40	80	80	80	60	0	20	45	50
Manganese	2.0	5	80	20	60	60	80	20	100	20	80	30
Molybdenum	5.0	5	0	0	0	0	0	0	0	100	0	25
Nickel	15	15	0	80	0	40	40	20	0	100	10	60
Mercury	30	10	80	0	60	0	40	80	40	20	55	25
Tin	75	25	0	0	0	0	20	0	0	0	5	0
Zinc	—	1	—	80	—	100	—	100	—	100	—	95
Bismuth	—	5	—	0	—	0	—	0	—	0	—	0
Calcium	—	0.1%	—	100	—	100	—	80	—	20	—	75
Titanium	—	NR[b]	—	100	—	100	—	100	—	100	—	100
Iron	—	NR[b]	—	100	—	100	—	100	—	100	—	100

[a] Not analyzed by test method.
[b] Not reported.

TABLE 9-6. METHOD PERFORMANCE RESULTS FOR ICP ANALYSIS

Metal	Method Blank (µg/Samples ± S.D.) n = 3	Method Control			Spiked Samples			
		Spiked Amount µg	% Recovery[a]	% RSD	Spiked Amount (µg)	% Rec	Spiked Amount (µg)	% Rec
Aluminum	0	2000	86	2	8295	86	7994	NR[b]
Selenium	0	210	105	5	871	86	840	93
Barium	8.8 ± 12	201	94	13	834	83	803	86
Antimony	0	200	98	3	830	85	799	96
Cobalt	0	200	105	4	830	87	799	75
Cadmium	0	201	101	3	834	96	803	88
Arsenic	0	210	95	3	871	87	840	89
Chromium	0.19 ± 0.87	203	107	10	842	89	811	85
Copper	0	210	97	4	834	80	803	85
Strontium	0.58 ± 0.43	200	128	49	830	83	799	64
Lead	22 ±30	1003	108	4	4160	94	4009	92
Manganese	0.04 ± 0.35	201	112	41	834	96	803	91
Molybdenum	0	200	98	2	830	83	799	89
Nickel	0	1002	89	5	4156	90	4005	84
Mercury	0	202	97	3	838	86	807	94
Tin	0.10 ± 1.2	200	102	4	830	77	799	85

a

$$\textit{Calculated}\ \frac{\textit{Measured Spiked } (\mu g) - \textit{Measured Unspiked } (\mu g)}{\textit{Amount Spiked}} \times 100\%$$

b All reported values less than zero.

c Not reported levels in unspiked triplicate samples were high and variable.

SECTION 10.0
QUALITY ASSURANCE\QUALITY CONTROL

10.1 OVERVIEW

Quality control (QC) and quality assurance (QA) activities were an integral part of this research program. The work was carried out following the guidelines and procedures detailed in the Work Assignment Revised Work Plan (10) and Revised Quality Assurance Project Plan (QAPP)(11). Much of the research conducted was a follow-up to previous work conducted on coatings (1). Quality assurance objectives, as outlined in the QAPP, are shown in Table 10-1.

Quality assurance activities that were conducted in support of this study included:

- Preparation of a Quality Assurance Project Plan,
- Meetings with work assignment staff on matters affecting data quality, and
- Systems audits of major study components.

Quality control samples (blanks, spiked controls, replicates) were analyzed as a part of this study. In addition, quality control procedures were included in the sampling and analysis phases of this study.

10.2 QUALITY ASSURANCE PROJECT PLAN

A (revised) QAPP(11) was prepared for this work assignment and covered all aspects of this work. The approved QAPP was used as a guide throughout the study to monitor QC procedures and adherence to study objectives.

Established test methods were utilized for sampling and analysis as summarized in Table 10-2. These procedures were supplemented with RTI standard operating procedures.

10.3 QUALITY CONTROL SAMPLES

10.3.1 Blanks

Blanks were prepared and analyzed along with samples to provide a measure of background contamination associated with sampling, handling and analysis. Banks were planned for each method as shown in Table 10-3. The table also includes completion rate and a cross-reference for results.

TABLE 10-1. SUMMARY OF QUALITY ASSURANCE OBJECTIVES

Parameter	Precision (%RSD)	Accuracy (%Recovery)	Completeness (%)
Volatiles Content			
Total Volatiles	≤1.5	ND[a]	≥95
Total Water	≤10	ND	≥95
Bulk Product Analysis			
VOC /SVOC[b]	≤20	80-100	≥95
TVOC	≤25	75-125	≥95
Metals (ICP)	≤20	80-120	≥95
Metals (XRF)	≤20	80-120	≥95
Small Chamber Emissions Testing			
VOC/SVOC[b]	NS	NS	≥95
TVOC	NS	NS	≥95
Aldehydes[c]	NS	NS	≥95
Emission Factors			
$mg/m^2 \bullet h$	NS	NA[e]	≥95
$mg/g \bullet h$	NS	NA	≥95

[a] Bias has not been determined for this method.
[b] For each of the 8 most abundant compounds identified.
[c] For five target analytes.
[d] Specific objectives were not set.
[e] No accuracy assessments will be made.

TABLE 10-2. SUMMARY OF TEST METHODS

Method Description	Method Reference	Analysis Method
Volatile Content of Paints		
Total Volatiles	ASTM D2369 [4]	Gravimetric
Water Content	ASTM D4017 [4]	Karl Fischer Titration
Bulk Product Analysis		
VOC/SVOC	Report [1]	GC/MS
Metals	NA[a]	XRF
Metals	Que Hee and Boyle [12]	ICP
Small Chamber Test for Emissions		
VOC/SVOC (latex)	Tichenor [13]	Tenax TA-GC/MS; GC/FID
VOC/SVOC (alkyd)	Tichenor [13]	Charcoal- GC/MS
Aldehydes	Winberry et al. [14]	HPLC

[a] Work Plan modified - XRF analysis performed by EPA using their procedures (Appendix E).

TABLE 10-3. BLANK SAMPLE SUMMARY

Method	Type	Number Planned/Reported	Results
Volatiles Content			
Total Volatiles	Weigh unused trays	2/2	Weight <0.0003 g
Water Content	Reagent	2/0	-
Bulk Product Analysis			
VOC/SVOC (Qual.)	Dilution Solvent	3/4	No VOCs/SVOCs detected above trace levels
VOC/SVOC (Quant.)	Dilution Solvent	3/4	No targets detected above quantitation limit
Metals (ICP)	Reagent Blank	3/3	Result given in Table 9-6
Metals (XRF)	Thin film substrate	3/0	Samples analyzed voluntarily by EPA using procedure given in Appendix E
Small Chamber			
Latex (SVOCs)	Chamber air/Tenax	11/6	No targets detected above the quantitation limit
Alkyd (VOCs)	Chamber air/Charcoal	11/6	No targets detected above the quantitation limit

10.3.2 Control Samples

Spiked samples were prepared, processed and analyzed along with samples to monitor losses associated with sampling and analysis. A summary of sample types planned and results is shown in Table 10-4.

10.3.3 Replicate Samples

Replicate samples are scheduled to provide precision estimates for the overall sampling and analysis process. For this study replicate tests were scheduled to provide precision estimates for the overall method. For Volatiles Content and Bulk Product Analysis replicate analysis of paint aliquots provides a measure of the analytical precision. A summary of precision evaluations is shown in Table 10-5.

10.4 QUALITY CONTROL PROCEDURES

10.4.1 Volatiles Content

Total Volatiles

QC Procedure	Result
Balance daily check weight; acceptance ≤1% deviation	Daily check not performed; analysis based on difference rather than absolute weight
Oven temperature; acceptance ± 5°C	Temperature verified

Total Water

QC Procedure	Result
System performance standard; Recovery must be 98-102%	Performance specifications met

10.4.2 Bulk Product Analysis

Qualitative Analysis (GC/MS)

QC Procedure	Result
Verify mass calibration using FC-43	Calibration verified
Manual review of GC/MS data	Completed by MS laboratory supervisor

TABLE 10-4. SPIKED CONTROL SAMPLE SUMMARY

Method	Type	Number Planned/Reported	Results
Volatiles Content			
Total Volatiles	None	0/0	Not applicable
Water Content	None	0/0	Not applicable
Bulk Product Analysis			
VOC/SVOC (Qual.)	None	0/0	Not applicable
VOC/SVOC (Quant.)	Dilution Solvent containing standards	3/8	Results given in Table 7-10 and 7-11
Metals (ICP)	Latex paint spiked with target metals	3/0	Sample analyzed voluntarily by EPA using procedure given in Appendix E
Metals (XRF)	Latex paint spiked with target metals	3/2	Results given in Table 9-6
	Spiked reagent blank	0/3	Results given in Table 9-6
Small Chamber			
Latex (SVOCs)	Spiked Tenax tubes	9/6	Results given in Table 8-11
Alkyd (VOCs)	Spiked Charcoal tubes	9/6	Results give in Table 8-6

TABLE 10-5. SUMMARY OF PRECISION MEASUREMENTS

Method	Type	Number Planned/Reported	Results
Volatiles Content			
Total Volatiles	Duplicates	12/12	Reported in Table 6-1
Water Content	Duplicates	12/12	Reported in Table 6-1
Bulk Product Analysis			
VOC/SVOC (Qual.)	None	0/0	Not applicable
VOC/SVOC (Quant.)	Duplicates	4/4	Reported in Tables 7-8 and 7-9
Metals (ICP)	Triplicate aliquot	20/20	Reported in Tables 9-3 and 9-4
Metals (XRF)	Triplicate aliquot	0/0[a]	Not applicable[a]
Latex (SVOCs)	Duplicate test	4/4	Reported in Tables 8-12, 8-26 to 8-31
Alkyd (VOCs)	Duplicate test	4/4	Reported in Tables 8-7, 8-16 to 8-22

[a] As modified, single analyses were performed by EPA.

Quantitative Analysis

Quality control procedures were carried out as described in the QAPP. These are summarized below. Calibration curve levels and number of points varied depending upon the estimated range of the specific analytes.

QC Procedure	Result
LATEX PAINTS (GC/MS)	
- 3-point calibration: %RSD for average RF < 30%	- 3-6 point calibration curve with < 30% RSD for average RF
- Verify mass calibration daily with FC-43	- Calibration verified
- Chromatographic performance check acceptance R > 1.5, TF > 0.5	- R = (2.1) 1,2-propanediol: ethylene glycol TF = (3.6) 1,2-propanediol
- Daily calibration check: acceptance < 25% difference	- < 25% difference in daily check
ALKYD PAINTS (GC/MS)	
- 3-point calibration: %RSD for average RF < 30%	- 4-point calibration curve with < 30% RSD for average RF
- Verify mass calibration daily with FC-43	- Calibration verified
- Chromatographic performance check acceptance R > 1.5, TF > 0.5	- R = (5.8) o-xylene:propylcyclohexane TF = (1) o-xylene
- Daily calibration check: acceptance < 25% difference	- < 25% difference in daily check

Metals Analysis

QC Procedure	Result
XRF Analysis	
Yearly multi-point calibration	Analysis was performed voluntarily by EPA (Appendix E) following their normal procedures. QC procedures not reported.
ICP Analysis	
Quarterly multi-point calibration - Verify linear range	3 point calibration verification performed during analysis
Calibration check standard after every 10th sample; acceptance ≤10% Difference	Calibration check standards (blank and standard) every fifth sample within ±10% except ±15% for As, Se, Sn, Hg (poor ICP elements)

10.4.3 Small Chamber Emissions Testing

Emission Factors (Chambers)

Parameter	Requirement	Result
Temperature	23 ± 1 °C	Verified for all tests
Relative Humidity	50 ± 5% RH	Verified for all tests
Air Exchange Rate	1.0 ± 0.05 per hour	Verified for all tests

Sample Analysis (GC/MS)

Quality control procedures were carried out as described in the QAPP. These are summarized below. Calibration curves levels and number of points varied depending upon the estimated range of the specific analytes.

QC Procedure	Result
LATEX PAINTS (GC/FID)	
- 5-point calibration: %RSD for average RF < 30%	- 5-point calibration curve, 6-point for ethylene glycol with < 30% RSD for average RF except diethylene glycol
- Verify mass calibration daily with FC-43	- Calibration verified
- Chromatographic performance check acceptance R > 1.5, TF > 0.5	- R = (4.1) 1,2-propanediol: ethylene glycol TF = (5.6) 1,2-propanediol
- Daily calibration check: acceptance < 25% difference	- < 25% difference in daily check except diethylene glycol
ALKYD PAINTS (GC/MS)	
- 5-point calibration: % RSD for average RF < 30%	- 9-point calibration curve with < 30% RSD for average RF
- Verify mass calibration daily with FD-43	- Calibration verified
- Chromatographic performance check acceptance R > 1.5, TF > 0.5	- R = (4.5) o-xylene: proplycyclohexane
- Daily calibration check: acceptance < 25% difference	- TF = (1.4) o-xylene < 25% difference in daily check

Sample Analysis (HPLC)

QC Procedure	Result
5-point calibration; acceptance, r^2 for curve ≥0.98	3-point calibration for selected analyses, all calibration curves met r^2 criteria
Daily calibration check; acceptance ≤25 % Difference	25% difference criteria met

10.5 QUALITY ASSURANCE

A summary of quality assurance activities, including systems audits, is shown in the Quality Assurance Statement (last page of this section).

Draft QA Statement
EPA Contract No. 68-D2-0131
ICF Work Assignment Number 1-18

Quality Assurance activities undertaken by the Analytical and Chemical Sciences (ACS) Quality Assurance Office in support of this program (RTI Project 5522-22) included:

- meetings with the Work Assignment Leader on matters affecting data quality,
- conducting periodic reviews and audits of the data measurement systems, and
- monitoring situations requiring corrective action.

The ACS QA Office conducts systems audits of current ACS studies to ascertain that data are being recorded properly, SOPs are being implemented, and that the results reported reflect the raw data of the study. Written reports of all reviews and audits are maintained by the ACS QA Officer, and results have been reported to the program management.

Inspection/Audit	Conducted	Reported
Instrument Log Notebook Inspection (ACS-SOP-815-003)	June 1993	July 19, 1993
Notebook Inspection (ACS-SOP-815-002)	September 1993	Sept. 23, 1993
SOP Review (ACS-SOP-110-001)	September 1993	Sept. 21, 1993
Training Files Inspection (ACS-SOP-110-002)	August 1993	Aug. 26, 1993

The ACS QA Officer conducted systems audits of this study as specified in the QAPP. Written reports of all audits are maintained by the ACS QA Officer, and the results have been reported to the Work Assignment Leader. These systems audits, and other reviews conducted in support of this study are listed below.

Inspection/Audit	Conducted	Reported
Preparation of testing materials/supplies	Not done	
Analytical measurement systems	March 3, 1994	IP
Data entry and processing	Feb. 10-Mar. 7, 1994	IP
Data validation	Feb. 10-Mar. 7, 1994	March 7, 1994
Document Review (ACS-SOP-130-003)	March 3-11, 1994	March 11, 1994

Doris Smith
ACS QA Officer

Date

SECTION 11.0

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APPENDIX A

RESULTS OF LITERATURE REVIEW FOR TEST METHODS

RESEARCH TRIANGLE INSTITUTE

Analytical and Chemical Sciences

January 29, 1993

Dr. Niren L. Nagda
ICF Work Assignment Manager
ICF Incorporated
9300 Lee Highway
Fairfax, VA 22031-1207

Dear Niren:

This letter reports the results of the literature search performed to identify additional/alternative methods for measuring emissions of aldehydes, volatile organic compounds (VOCs), or semi-volatile organic compounds (SVOCs) from liquid products and methods for determining the content of aldehydes, VOCs/SVOCs, or metals in liquid products. This work was performed under Task 1 of Work Assignment Number 1-18, "Determination of Test Methods for Interior Architectural Coatings," under EPA Contract No. 68-D2-0131.

To identify potential sources of information on additional or alternative methods, a computerized literature search was conducted using the DIALOG One Search System. Files that were searched included the following:

- Enviroline,
- Pollution Abstracts,
- NTIS,
- Inspec 2,
- Analytical Abstracts Online,
- CA Search,
- Energy Science & Technology, and
- Compendex Plus

A hierarchical searching method was used to limit the number of citations to be reviewed. Key words, or permutations of the words (e.g., paint*) that were used for metals included paint, coating, ICP, XRF, inductively, coupled, plasma, and x-ray fluorescence. For aldehydes, the keywords included paint, coating, aldehyde, ketone, formaldehyde, analysis, measurement, and detection. Keywords to search for methods for emissions testing included paint, coating, VOC, volatile, organic, emission, test, measure, chamber, and chambre. The search was not limited by year of publication or by country of publication. Potentially relevant citations were printed and reviewed. Copies of selected publications and reports were ordered, reviewed at local libraries, or collected from reports and publications available at Research Triangle Institute (RTI).

In addition to the computer search, reports were reviewed in proceedings from meetings and symposia such as the International Indoor Air Quality and Climate conferences,

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annual American Society of Heating and Refrigerating Engineers (ASHRAE) indoor air conferences, and American Waste Management Association (AWMA) meetings. A review of analytical techniques applicable to the examination of coatings is published every two years by the journal Analytical Chemistry. The reviews for the years from 1981 to 1991 were examined to identify relevant citations.

Telephone calls were also made to selected researchers in the U.S. who have published papers related to emissions testing or characterization of indoor air contaminant sources.

The literature search has not identified any additional or alternative methods that we would recommend for inclusion in this work assignment. As discussed below, there is an alternative emissions chamber, the FLEC, that may be potentially useful for measuring emissions from paints and other liquid products. However, we do not recommend evaluating it in this work assignment because initial evaluations are being planned by Dr. Tichenor at EPA. Information was not identified in the literature search on sampling or analysis methods that should be substituted for those that we have selected, as outlined in the Work Plan and Quality Assurance Project Plan, for VOCs/SVOCs, aldehydes, or metals. The following discussion summarizes the results of our literature search in four areas: (1) methods for determining emissions of VOCs/SVOCs and aldehydes, (2) methods for determining the VOC/SVOC content of paints, (3) methods for determining the aldehyde content of paints, and (4) methods for determining the content of metals in liquid paints.

Methods For Determining Emissions of VOCs/SVOCs and Aldehydes

During the last decade, researchers in Europe and the United States have been active in the development of methods for determining emissions of volatile organic compounds from both solid and liquid materials that are used indoors. Much of the early work was done to characterize formaldehyde emissions from products such as plywood, pressed wood products, and urea-formaldehyde resins using large room-size chambers. More recently, development work has been directed toward use of small chambers for VOC emissions measurements.

There are numerous reports in the literature of emissions measurements obtained with chambers of various sizes and construction materials. The diversity of the construction characteristics of emissions test chambers is best summarized in the recent report by DeBortoli and Colombo (1992) that describes the results of an international comparison experiment on the determination of VOCs emitted from indoor materials through small test chambers. Twenty-three chambers used in the experiment ranged in capacity from 0.004 to 1.475 m^3. Seventeen chambers were constructed of stainless steel, one of plated steel, and the others were glass. For PVC tile, the inter-laboratory variability, expressed as the relative standard deviation for concentrations of the emissions of the target compounds measured two hours after t_o, was less than 45% for all of the participating laboratories. But for a wax sample, the RSDs ranged from 45 to 160% for the target compound concentrations. The results showed acceptable method precision for the solid material, but large variability between the laboratories for measurements of emissions from the liquid product. However, analysis of the data indicated that the chamber capacity did not introduce any systematic difference in the results. Nor could any significant differences in the results be attributed to the chamber wall material. This suggests that, although there are differences between emission chambers, instrumentation, and test methods, there may not be substantial difference in emissions test results with different chambers.

Wolkoff and his co-workers (1991) have reported development of the Field and Laboratory Emission Cell (FLEC) for emissions measurements. This is a dramatically different design for an emission chamber. It has a capacity of only 35 cm^3 and a maximum test surface area of 0.0177 m^2. The chamber is operated at 171 air exchanges per hour compared to the 0.5 to 2 air exchanges per hour typically used in small chamber testing. This micro emission cell showed satisfactory correlation with a 234 L chamber for tests with vinyl floor carpet. It is potentially useful for determining emissions of liquid products. It is our understanding that Dr. Bruce Tichenor's group at the EPA Air and Energy Engineering Research Laboratory (AEERL) has ordered the FLEC for evaluation. We do not recommend that it be included for evaluation in this work assignment because preliminary evaluations have not yet been initiated by Dr. Tichenor.

With the exception of the FLEC, we did not identify any new emissions test methods. Researchers use small chambers and large (room-size) chambers for quantitating emissions. Headspace analysis or direct analysis of products are used to identify the target analytes for quantitation.

Small chamber test methods have been used for measuring emissions of VOCs, SVOCs, and aldehydes. VOCs have been measured most frequently (Tichenor and Mason, 1988). Reports of emissions of less volatile organic compounds from household products have been reported (e.g., Clausen et al., 1991 and Colombo et al., 1990). Tenax has been widely used for collection of emissions from solid and wet products, although Carbotrap and other charcoal-based sorbents have been used (Clausen et al., 1991; Volkl et al., 1990; Black et al., 1991; and others). Work has been performed to evaluate the performance of various sorbent materials. The charcoal based sorbents are well-suited for the collection of VOCs. Recovery by solvent extraction is good for a wide range of compounds. Collection of air samples on carbon-based sorbents with subsequent thermal desorption for analysis has been shown to be a suitable method for many volatile compounds (Mason et al., 1992), but not all compounds can be recovered from the sorbent by thermal desorption. Data were not found on the performance of different sorbents for the less volatile analytes that have been identified in latex paints (e.g., Texanol). Although Clausen and his coworkers (1991) used Tenax TA to collect emissions from latex paint, they did not report either the percent recovery of the analytes from spiked control cartridges nor the recovery of the higher molecular weight, less volatile, compounds from the chamber. In summary, the literature review did not identify performance data for sorbents that would suggest selection of alternatives to the Tenax TA (for VOCs/SVOCs emitted from latex paint) and activated carbon (for VOCs emitted from alkyd paint) proposed for evaluation in this study.

Formaldehyde has been collected in numerous studies using impingers containing sodium bisulfite for subsequent analysis by the chromotropic acid method (NIOSH, 1977). Although this is an excellent method for determination of formaldehyde, collection of air samples on silica gel coated with 2,4-dinitrophylhydrazine (DNPH) with subsequent analysis by high performance liquid chromatography (HPLC) is now widely used. The method has the advantage of lower detection limits, sample collection and analysis are easier to perform, and the same method can be used to determine a number of different carbonyl compounds. The fact that the method can be used for determination of a number of different aldehydes is one of the most important advantages of the method. The method is widely used for ambient air sampling and has been used for emissions testing, including tests to determine emissions from adhesives, floor cleaning products, waxes, and deodorizers (Person et al., 1990). No alternative methods that were more suitable for sampling and analysis of emissions of aldehydes from paints were identified in this literature search.

Methods For Determining the VOC/SVOC Content of Paints

Volume 06.01 of the Annual Book of ASTM Standards (ASTM, 1992) contains the following methods and practices:

- D4457 - Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph.
- D3271 - Direct Injection of Solvent-Reducible Paints Into a Gas Chromatograph for Solvent Analysis.
- D3272 - Vacuum Distillation of Solvents From Solvent-Reducible Paints for Analysis.
- D3168 - Qualitative Identification of Polymers in Emulsion Paints.

Methods D4457 and D3271 are packed column methods, which are not as suitable for analysis of paints as the capillary column methods that we used in the previous study and that will be used in this work assignment. Method D 3168 is a pyrolysis method intended to identify monomers in paint and is not intended to identify volatile emissions from coatings. Method D3272 is an alternative to direct injection. Results from our previous evaluation of methods demonstrated that direct injection was an appropriate method for identifying the VOCs that would be emitted from paint. Therefore, distillation to separate the solvents from the solids is not necessary. Olson and co-workers (1987) reported a method for determining solvent formulations of paints using a Unacon 810A with a pyroprobe. An aliquot of paint was introduced into the tube furnace and heated to 150 °C. The vaporized solvents were collected on the Unacon concentrator traps, then analyzed by GC/FID. The precision of the method was generally better than ± 10% (%RSD) and recoveries ranged from 76 to 120%. This method represents an alternative method that could be employed for certain liquids if they are not amenable to analysis by direct injection.

Another method that has been proposed for the determination of VOCs in paints is the method developed at RTI (Petersen et al., 1991) as an alternative to ASTM methods D2369 and D4017. The method was evaluated in our previous study. The performance of the method was excellent for determining total volatile organic compound and water concentrations. The charcoal sorbent was extracted for qualitative determination of the VOCs emitted during drying of the paint. Some of the most abundant VOCs in the alkyd paint were identified. But the method was not suitable for determination of the less volatile compounds emitted from the latex paint. The method, however, is still under development for the purpose of identifying the individual VOCs in the paints. It was not recommended for evaluation in this work assignment.

Methods for Determining the Content of Aldehydes in Liquid Paints

Carbonyl compounds have been analyzed by gas chromatography as their phenylhydrazones, 2,4-dinitrophenylhydrazones, and oximes (summarized by Peltonen, et al., 1984). A method of analysis of formaldehyde by GC/MS using deuterated internal standards has also been reported (McGuire et al., 1991). Peltonen and his coworkers (1984) reported a method for the separation and determination of dimethone adducts of aldehydes by GC.

HPLC has been used for the separation and detection of a number of carbonyl compounds derivatized with DNPH (as described in Method TO-11, Winberry et al., 1988). HPLC analysis of air samples collected on DNPH coated silica gel will be used in this work assignment. Selim (1977) reported on the quantitative conversion of propionaldehyde to its 2,4-dinitrophenylhydrazone. The quantitative conversion of the aldehydes and the low detection limits with this method make it advantageous. Methods for derivatization of aldehydes for the preparation of calibration standards are described in TO-11. Waters Associates also has published a method for preparing derivatives using their DNPH reagent. The method proposed for this work plan is based on direct derivatization of the aldehydes in paints with the Waters reagent or derivatization of a solution of the paint in an appropriate solvent.

The literature search did not identify methods for determining aldehydes in paints which are more appropriate than the HPLC method.

Methods for Determining Metals in Liquid Paints

Numerous methods have been published for the determination of metals in solid and liquid matrices. A number of standardized methods for digestion of samples with subsequent analysis by atomic absorption spectroscopy (AAS) have been published as ASTM methods and as EPA methods (e.g., EPA Methods for Chemical Analysis of Water and Wastes, U.S. EPA, 1983). AAS methods, however, are for determination of a single element. To meet the objectives of EPA/ORIA and OPPT, multi-element methods are desired. The selection of x-ray fluorescence spectroscopy (XRF) and inductively couple plasma (ICP) spectroscopy are appropriate methods for evaluation in this work assignment because both are applicable to multi-element analyses of paints. Que Hee and Boyle (1988), for example, have evaluated ICP for determination of metals in a variety of matrices, including dry paint samples. They reported good precision and accuracy for a microwave digestion/ICP method for most of the 22 elements that were determined by the method. Binstock and coworkers

(1991) reported similar results for the microwave method developed by RTI. The method should be suitable for liquid paint samples. ASTM method D4764 is a method for determination of titanium by XRF. The method involves determination of titanium in liquid paints by analysis of a sample prepared as a thin film. The method will serve as the basis for the XRF method to be used in this study for multi-element determinations. Because XRF and ICP are the most appropriate methods to be evaluated in this work assignment, a comprehensive review of AAS methods is not included in this report.

Summary

The literature review has not identified additional methods that we would recommend for further evaluation in this work assignment. Because of the tight time schedule for reporting on the literature search, a few of the relevant papers/reports have not yet been received for comprehensive review. However, based on the titles of the citations and our current information on available sampling, analysis, and emission test methods, we do not believe that these citations will identify additional methods that should be incorporated for evaluation in the current work assignment. We will be reviewing additional information to determine if any alternative methods should be considered, particularly for the determination of aldehydes in the liquid paints.

References cited in this letter report are included as an Attachment.

Submitted by:

Roy C. Fortmann

Roy C. Fortmann
RTI Work Assignment Leader

Approved by:

for EDP

Edo D. Pellizzari
Vice-President
Analytical and Chemical Sciences

cc: Dr. D. Naugle, Program Manager
5522-22 File

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RESEARCH TRIANGLE INSTITUTE

Analytical and Chemical Sciences

March 5, 1993

Dr. Niren L. Nagda
ICF Work Assignment Manager
ICF Incorporated
9300 Lee Highway
Fairfax, VA 22-31-1207

Dear Niren:

As suggested by John Girman, I have made some additional telephone contacts to determine if any relevant data are available on recovery of Texanol and other latex paint analytes from Tenax TA or other sorbent media. This work was performed under Task 1 of Work Assignment Number 1-18, "Determination of Test Methods for Interior Architectural Coatings," under EPA Contract NO. 68-D2-0131.

Al Hodgson of Lawrence Berkeley Laboratory is about to begin some work on the recovery of Texanol from the multi-sorbent traps, but does not have any data at this time. He uses the Envirochem tubes and a Unacon desorber/concentrator similar to the unit we use. Al indicated that he has experienced some problems obtaining a good calibration curve for butoxyethanol using the multi-sorbent tube/thermal desorption system, but has not identified the cause of the problem.

Charlie Weschler and Helen Shields have experience with the measurement of Texanol using the 3M badge. The collection media in the badge is a filter impregnated with charcoal. The carbon disulfide extraction apparently provides good recovery. They do not have experience with Tenax.

Marilyn Black uses the Carbosieve/Carbopack multisorbents. She hasn't worked with Texanol. But she has performed recovery tests for 2-(2-butoxyethoxyethanol), one of the latex paint analytes. She says recovery is approximately 75% with the thermal desorption method.

I also talked to Peder Wolkoff at the National Institute of Occupational Health in Denmark. He was one of the authors of the paper on long-term emissions of VOCs from latex paint (Indoor Air, 4:562-576, 1991). They used sampling tubes containing 200 mg of Tenax TA and a Perkin-Elmer system for thermal desorption. Peder advised me that they have not done tests to determine the recovery of individual VOCs from the sampling cartridges. Instead, they do what he referred to as "total recovery" for the method by performing their calibration using Tenax TA cartridges spiked with the analytes. The standards are prepared in methanol, then loaded onto the front of the Tenax bed of the cartridge. Helium is then passed through the

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cartridge at 50 mL/min for 3 minutes. With this approach, if the recovery from the cartridge is not dependent of the mass of analyte loaded onto the sorbent bed, you will obtain a linear calibration curve over your dynamic range. Recovery of Texanol from air samples collected on the cartridge is assumed to be the same as that from the spiked cartridges used for calibration. He indicated that they get a good linear calibration and have had no problems with the major compounds in the latex paint emissions.

Preparation of calibration curves using standards loaded on the sampling cartridges is our standard practice when performing thermal desorption/GC/MS with Tenax or multi-sorbent tubes. We do not inject liquid solutions of the standards directly onto the GC column to develop our calibration curves. Our procedure, therefore, is the same as that of Wolkoff. For this Work Assignment we will perform initial recovery tests to determine that the recovery of the target analytes is adequate. This is done by comparing the response of the instrument for standards in solution injected onto the column against the response for standards thermally desorbed from spiked Tenax cartridges.

If you have any questions about our procedures, we can discuss then on March 11, 1993 when you and Pauline Johnston visit our facility.

Sincerely,

Roy C. Fortmann

Roy C. Fortmann
RTI Work Assignment Leader

cc: Dr. D. Naugle, Project Office

APPENDIX B

PAINT SELECTION MEMOS

RESEARCH TRIANGLE INSTITUTE

RTI

Analytical and Chemical Sciences

April 23, 1993

4-26-93 Change Sherwin Williams to Pro Mar 400 paints.

Dr. Niren L. Nagda
ICF Work Assignment Manager
ICF Incorporated
9300 Lee Highway
Fairfax, VA 22-31-1207

Dear Niren:

As I discussed with you this morning, I have collected additional information about the Glidden and Sherwin-Williams paints that will be used for testing in the Work Assignment. I would like to proceed with purchase of the paints after Pauline Johnston has a chance to review my proposed selection of paints. The procedure for selection will be as outlined in the Work Plan with one minor modification, as will be described below.

The paints that will be purchased will be a medium to high grade, based on cost. Both the Glidden and Sherwin-Williams paints that I have selected are the "most popular" choice of homeowners according to staff at the retail outlet. ~~The paints that have been selected are not "contractors" paints (except for the gloss paint) nor are they intended for "industrial"~~ use. The Sherwin-Williams latex flat, latex semi-gloss, alkyd flat, and alkyd semi-gloss are the ~~Classic 99~~ Pro Mar 400 series. The Sherwin-Williams latex gloss and alkyd gloss paints are the Pro Mar ~~200~~ 400 series, a contractors paint, because the gloss paints are not manufactured in the Classic 99 series or other "homeowner" paints. All Sherwin-Williams latex paints contain the vinyl polymer. Glidden has all six types of paints in a medium to high grade, but the names vary for each type of paint. The latex flat paint will be the Spread Satin series and will be the same paint as used in the previous testing. Glidden has the vinyl polymer only in the latex flat paint; it is not used in the semi-gloss or gloss.

if available

All of the six types of paints can be purchased in any of the manufacturer's colors. I have obtained paint "chips" from each manufacturer. Glidden has about 600 colors. Sherwin-Williams has over 800 colors. The Sherwin-Williams paint chips use a letter code to indicate the base paint that is tinted. An "X" indicates that a neutral colored base is used. Each paint chip usually has five colors of varying tint-strength that use the "X" base and two darker colors that are produced by adding tint to a colored base. The Glidden paint chips each show four similar colors (with varying amounts of tint), but they do not indicate the base that is used.

As outlined in Section 3.1 of the QAPP, paints for bulk product and emissions testing will be randomly selected after stratification into six major color groups (green, yellow, blue, red, purple, and orange). Each color on the paint chips will be numbered within each color

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group. A random number generator will be used to select the color for each of the 12 paint types listed in Table 1 of the Work Plan. I have also randomly assigned each of the twelve paints to a color group using a random number generator. The paint type assigned to each color group is as follows:

Color Group	Sherwin-Williams	Glidden
Green	Alkyd gloss	Alkyd semi-gloss
Yellow	Alkyd flat	Alkyd flat
Blue	Alkyd semi-gloss	Latex semi-gloss
Red	Latex gloss	Latex flat
Purple	Latex semi-gloss	Alkyd gloss
Orange	Latex flat	Latex gloss

The eight additional paints to be used only for metals analyses (in addition to the twelve paints listed above) will be colors that are randomly selected from all available colors, without stratification by color group. I have randomly selected the following additional paints for metals analysis:

Sherwin-Williams	Glidden
Alkyd flat	Alkyd flat
Alkyd semi-gloss	Alkyd gloss
Latex flat	Latex gloss
Latex semi-gloss	Latex semi-gloss

As I discussed with you, I believe all of the available colors on the paint chips should be eligible for selection. However, I would like to add the criterion that no more than one paint can be selected from any paint chip. I believe this is necessary because paints with colors on the same chip may vary only in the amount of tint that was added. This would reduce the diversity of paints included in the study.

As you suggested, I will telefax a copy of this letter to Pauline Johnston for her review.

Sincerely,

Roy C. Fortmann

Roy C. Fortmann
RTI Work Assignment Leader

cc: Ms. Pauline Johnston, EPA
Dr. D. Naugle, RTI Project Office

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
AIR AND RADIATION

TECHNICAL DIRECTIVE (TD# 3 for WA# I-18)

Date: April 29, 1993

From: Pauline Johnston
EPA Work Assignment Manager

To: Niren Nagda
ICF Work Assignment Manager

This technical directive requests work under the contract, work assignment, and task listed below.

Contract No.:	68-D2-0131
Work Assignment:	I-18
Task Number: *(if appropriate)*	Task 3, Part 1
Description of Work:	The selection of paints will be made in accordance with the attached April 23, 1993, letter from Roy Fortmann to you, with three changes as discussed in our conference call earlier today. The changes are as follows:

- Instead of choosing the Sherwin Williams Classic 99 and Pro Mar 200 series paints, the Sherwin-Williams paints will be from the Pro Mar 400 series. In this way, half the paints chosen will be "homeowner" paints and half will be "contractor" paints. In addition, the contractor paint will be from the intermediate grade series that is used in the greatest quantities by contractors. All of these paints contain the vinyl polymer.

- When selecting colors for the Pro Mar 400 series, the darkest color on a color swatch will not be used since these colors are usually not available in this paint series. If the darkest color on a swatch is chosen, the color will be reselected.

- Colors that are too difficult to put into a particular color group (e.g., white, gray, black, brown, some teals, etc.), representing about 20% of the total colors, will be excluded when choosing from the six major color groups for the first 12 paints samples. However, the remaining eight sample colors will be chosen from all the available colors.

cc: Project Officer
Contracting Officer

RESEARCH TRIANGLE INSTITUTE

Analytical and Chemical Sciences

May 10, 1993

Dr. Niren L. Nagda
ICF Work Assignment Manager
ICF Incorporated
9300 Lee Highway
Fairfax, VA 22-31-1207

Dear Niren:

As I advised you in our telephone conversation today, the selection method described in my letter dated April 23, 1993 for the eight additional paints to be used for metals analysis only differs from the method described in Section 3.1 of the Quality Assurance Project Plan (QAPP). In the QAPP we state, in the second bullet, the numbers of each type of paint that will be selected for each manufacturer. This statement indicates that the paints for metals analysis only will include a flat latex, a semi-gloss latex, a semi-gloss alkyd and a gloss alkyd from each manufacturer. The original intent of this selection method was to obtain the types of paints that are most widely used (i.e., alkyd flat and latex gloss paints represent less market share). However, in my letter dated April 23, 1993, I proposed a simple random selection. When I did the random selection, the types of paints that were selected were different than those stated in the QAPP. Based on currently available information, we do not know if the metals content will differ for different gloss types. Therefore, I believe the random selection process proposed in my letter is the most appropriate method to select the paints.

We have also learned that the Sherwin-Williams Pro-Mar 400 series is limited to the latex flat, latex semi-gloss, and alkyd semi-gloss types of paints. The Pro-Mar 200 series, however, includes all of the types of paints (latex and alkyd in flat, semi-gloss, and gloss). The Pro-Mar 200 series is the "top-of-the-line" (i.e., most expensive) paint. I suggest that we use paints from the Pro-Mar 200 series for testing in this Work Assignment.

Please advise me of your response to these issues and provide a technical directive to me regarding these matters. Feel free to call me if you would like to discuss these issues. We want to procure these paints as soon as possible.

Sincerely,

Roy C. Fortmann

Roy C. Fortmann
RTI Work Assignment Leader

cc: Ms. Pauline Johnston, EPA
Dr. D. Naugle, Project Office

Post Office Box 12194 Research Triangle Park, North Carolina 27709-2194
Telephone 919 541-6507 FAX: 919 541-7208

SENT BY: ICF INCORPORATED

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
AIR AND RADIATION

TECHNICAL DIRECTIVE (TD#4 for WA# I-18)

Date: May 12, 1993

From: Pauline Johnston PJ
EPA Work Assignment Manager

To: Niren Nagda
ICF Work Assignment Manager

This technical directive requests work under the contract, work assignment, and task listed below.

Contract No.:	68-D2-0131
Work Assignment:	I-18
Task Number: *(if appropriate)*	Task 3, Part 1
Description of Work:	The proposed changes to the paint selection criteria, as detailed in the attached letter from Dr. Roy Fortmann to you dated May 10, 1993, are reasonable. Therefore, proceed with a random selection of the eight additional types of paint for metals analysis as detailed in the first paragraph of the letter. Also, use the Pro-Mar series 200, rather than the Pro-Mar series 400, paints.

cc: Project Officer
Contracting Officer

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APPENDIX C

EXAMPLE CALIBRATION CURVE FOR QUANTITATING VOC EMISSIONS FROM ALKYD PAINT SAMPLES

Calibration Report

CBM21

Title: ALKYD CHARCOAL TEST SAMPLES IN CS2 WITH O-XYLENE-D10 AS I.S.
Calibrated: 940215 09:29

Compound	Files:	>09149 RF 25.00	>09150 RF 50.00	>09151 RF 100.00	>09152 RF 250.00	>09158 RF 500.00	- RF 1000.0	>09154 RF .500	>09155 RF 1.00	>09156 RF 2.50	>09157 RF 10.00	RF (avg)	% RSD
TOLUENE	91	2.75012	2.97379	2.93922	3.15177	2.57010	-	2.67490	2.98360	3.12013	2.75025	2.87932	7.015 (C
TOLUENE	92	1.56655	1.64079	1.62106	1.83786	1.71545	-	1.51460	1.64529	1.73975	1.56598	1.64970	6.097 (C
M,P-XYLENE	91	2.21536	2.37113	2.24327	2.06377	1.48318	-	2.08347	2.27202	2.33790	2.21399	2.14268	12.482 (C
M,P-XYLENE	106	1.10386	1.17638	1.12645	1.17927	.90759	-	1.02837	1.10068	1.20206	1.11731	1.10466	8.191 (C
NONANE	85	.50291	.54304	.51466	.56059	.51626	-	.35980	.43122	.49261	.50317	.49158	12.421 (C
NONANE	57	1.30552	1.43077	1.35413	1.58107	1.33727	-	1.10040	1.24209	1.31554	1.28225	1.32767	9.868 (C
O-XYLENE	91	2.24419	2.45938	2.28358	2.50995	2.02376	-	2.17484	2.32676	2.42462	2.28880	2.30399	6.530 (C
O-XYLENE	106	1.04300	1.10876	1.07079	1.14680	1.08005	-	.96047	1.04090	1.14392	1.09754	1.07691	5.381 (C
PROPYL CYCLOHEXANE	83	1.72280	1.83355	1.77372	1.92949	1.64848	-	1.60465	1.66856	1.80461	1.76266	1.74984	5.775 (C
PROPYL CYCLOHEXANE	55	1.26416	1.32851	1.26818	1.48299	1.21087	-	1.01048	1.27686	1.26399	1.25499	1.26234	9.680 (C
3- & 4-ETHYL TOLUENE	105	2.55083	2.72021	2.68029	2.58439	1.91664	-	2.40332	2.60660	2.69237	2.57891	2.52595	9.787 (C
3- & 4-ETHYL TOLUENE	120	.75571	.80854	.76697	.81668	.73657	-	.65861	.75260	.82206	.78345	.76680	6.602 (C
1,3,5-TRIMETHYLBENZENE	105	2.20976	2.32881	2.17905	2.34385	1.94173	-	1.93152	2.19024	2.29272	2.22023	2.18199	6.927 (C
1,3,5-TRIMETHYLBENZENE	120	1.09853	1.20292	1.11939	1.24368	1.03099	-	.98853	1.08187	1.18217	1.12781	1.11954	7.286 (C
DECANE	85	.41299	.44614	.42072	.45610	.41519	-	.26006	.37910	.40056	.41740	.40092	14.334 (C
DECANE	57	1.49838	1.67285	1.57173	1.66841	1.49240	-	1.26053	1.47266	1.43744	1.44283	1.50191	8.445 (C
2-ETHYL TOLUENE	105	2.53453	2.81254	2.56128	2.91797	2.16690	-	2.31754	2.58368	2.77387	2.61728	2.58729	9.154 (C
2-ETHYL TOLUENE	120	.76988	.82038	.76132	.81169	.76645	-	.67309	.76841	.80473	.80213	.77534	5.721 (C
1,2,4-TRIMETHYLBENZENE	105	2.09620	2.48200	2.19192	2.33263	1.93068	-	1.93132	2.14747	2.26486	2.18633	2.17371	8.191 (C
1,2,4-TRIMETHYLBENZENE	120	1.00693	1.04396	.96681	1.14329	.98692	-	.80211	.96062	1.07964	1.02046	1.00119	9.426 (C
1,2,3-TRIMETHYLBENZENE	105	2.03628	2.20477	2.03710	2.36083	1.81962	-	1.79380	1.98137	2.14026	2.02584	2.04443	8.695 (C
1,2,3-TRIMETHYLBENZENE	120	.87246	.90738	.87670	.93248	.86952	-	.70337	.83461	.93667	.89043	.86929	8.055 (C
2-METHYLDECANE	85	.40501	.45417	.40790	.44824	.39128	-	.23553	.33747	.41598	.40364	.38880	17.139 (C
2-METHYLDECANE	57	1.23429	1.48697	1.48508	1.45632	1.26208	-	1.11868	1.25837	1.31895	1.21956	1.31559	10.007 (C
TRANS-DECAHYDRONAPHTHALENE	96	.52426	.57921	.52049	.54536	.48089	-	.38988	.50712	.57660	.54379	.51862	11.107 (C
TRANS-DECAHYDRONAPHTHALENE	138	.69044	.70982	.65876	.72864	.66605	-	.54864	.61065	.72349	.67660	.66812	8.648 (C
UNDECANE	85	.43409	.46426	.43377	.47647	.42351	-	.30580	.36924	.42743	.43006	.41829	12.335 (C
UNDECANE	57	1.49023	1.80033	1.67006	1.72297	1.52251	-	1.31378	1.45823	1.59334	1.48587	1.56192	9.611 (C
PENTYLCYCLOHEXANE	83	1.76190	2.03120	1.81377	1.99828	1.63831	-	1.51588	1.73408	1.90022	1.83396	1.80307	9.129 (C
PENTYLCYCLOHEXANE	55	1.19079	1.24935	1.24656	1.33068	1.14177	-	.98292	1.09024	1.24530	1.13374	1.17904	8.835 (C
N-DODECANE	85	.48383	.53019	.47260	.51768	.43332	-	.27336	.39066	.48007	.47718	.45099	17.407 (C
N-DODECANE	57	1.57881	1.75955	1.61296	1.73332	1.42031	-	1.13389	1.32019	1.55480	1.55386	1.51863	13.093 (C

RF - Response Factor (Subscript is amount in ng/uL)

$\overline{RF}$ - Average Response Factor

%RSD - Percent Relative Standard Deviation

APPENDIX D

EMISSION RATE DATA

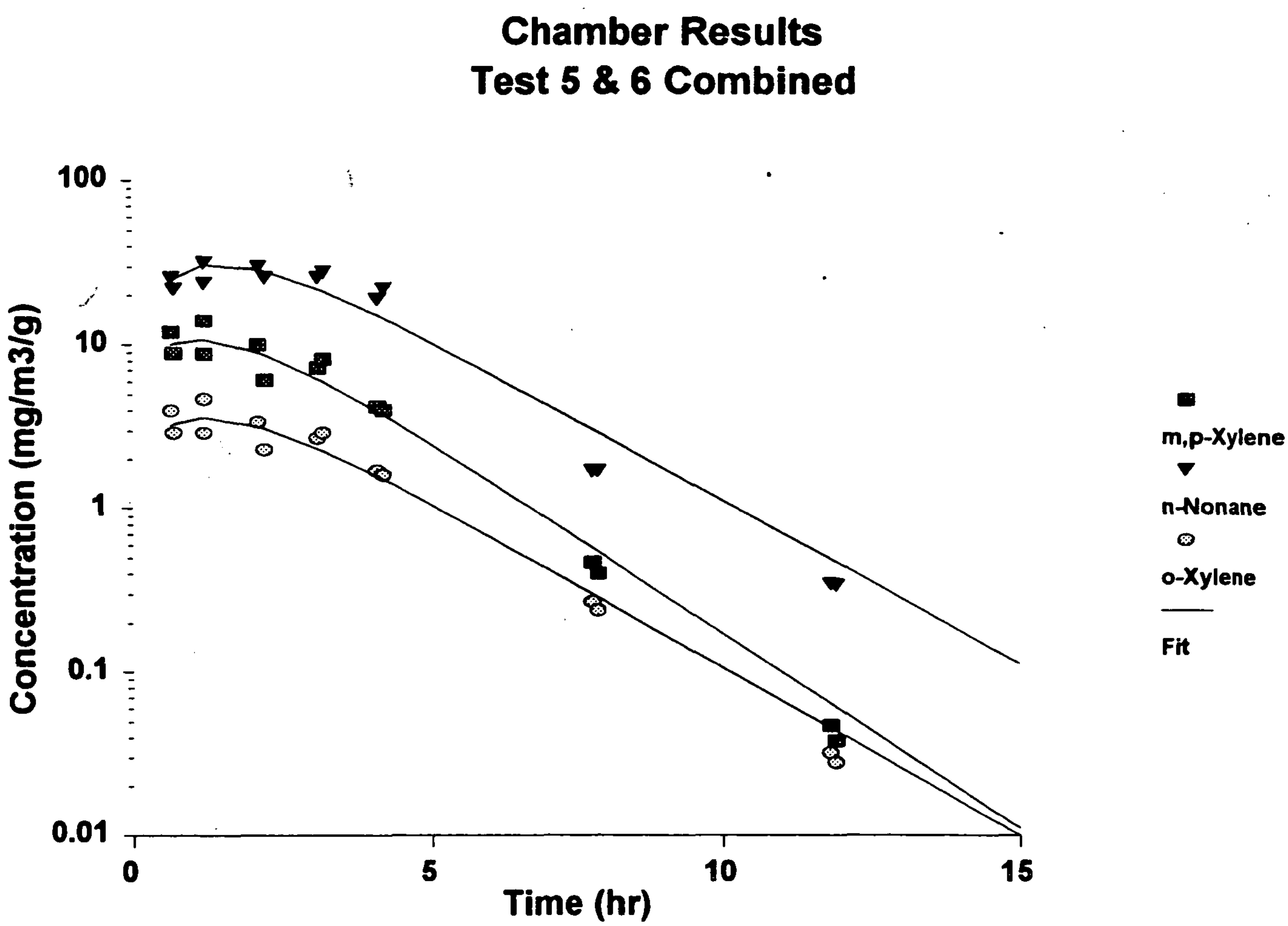
ALKYD PAINTS

Chamber	VOC	Recovery	Study						Vol	0.05276
	TEST 5 & 6 Combined									
Time hr	m,p-Xylene	n-Nonane	o-Xylene	Propylcycloh	3&4-Ethyltol	1,3,5-Trimet	n-Decane	2-Ethyltoluen	1,2,4-Trimet	1,2,3-Trimet
0.65	12	26	4	9.3	5.1	1.7	40	1.5	5.3	1.4
1.2	14	32	4.7	11	6.9	2.3	54	2	7.4	2.1
2.1	10	30	3.4	11	6.2	2.3	59	1.9	7.2	2.1
3.1	7.2	26	2.7	11	6.1	2.2	63	1.9	7.4	2.2
4.1	4.2	19	1.7	7.4	4.7	1.9	57	1.5	6.1	1.9
7.8	0.47	1.7	0.27	0.71	1.4	0.63	15	0.16	2.1	0.94
11.8	0.047	0.35	0.032	0.23	0.44	0.28	9.3	0.15	1.1	0.52
24.6							0.065		0.02	0.026
0.7	8.9	22	2.9	8.9	4.4	1.6	37	1.4	4.8	1.3
1.2	8.8	24	2.9	7.9	4.6	1.6	41	1.4	4.9	1.3
2.2	6.1	26	2.3	9.1	5.4	2	60	1.6	6.6	1.9
3.2	8.2	28	2.9	9.6	5.6	2.1	55	1.7	6.4	1.8
4.2	4	22	1.6	9.2	5	2	63	1.6	6.5	1.9
7.9	0.4	1.7	0.24	0.59	1.4	0.68	17	0.25	2.3	1
11.9	0.038	0.34	0.028	0.21	0.45	0.28	11	0.18	1.2	0.56
24.9							0.055		0.023	0.026
Sumsq	1.955	3.248	1.078	2.336	1.027	0.582	4.543	0.911	1.160	0.633
~~Sumsq/C0~~ Std	0.059	0.033	0.096	0.064	0.050	0.076	0.020	0.145	0.043	0.080
S0 (mg/hr-g)	1.050E+00	3.189E+00	3.416E-01	1.127E+00	5.484E-01	1.855E-01	4.866E+00	1.783E-01	5.790E-01	1.528E-01
K (/hr)	5.534E-01	4.594E-01	4.744E-01	4.366E-01	2.844E-01	2.327E-01	2.299E-01	3.498E-01	2.213E-01	1.640E-01
C0	4.186E+00	0.000E+00	1.234E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Emission (mg/g)	2.30	6.94	0.86	2.58	1.93	0.80	21.17	0.51	2.62	0.93

S(t) = S0 exp(-kt) with C0 = Concentration at t=0

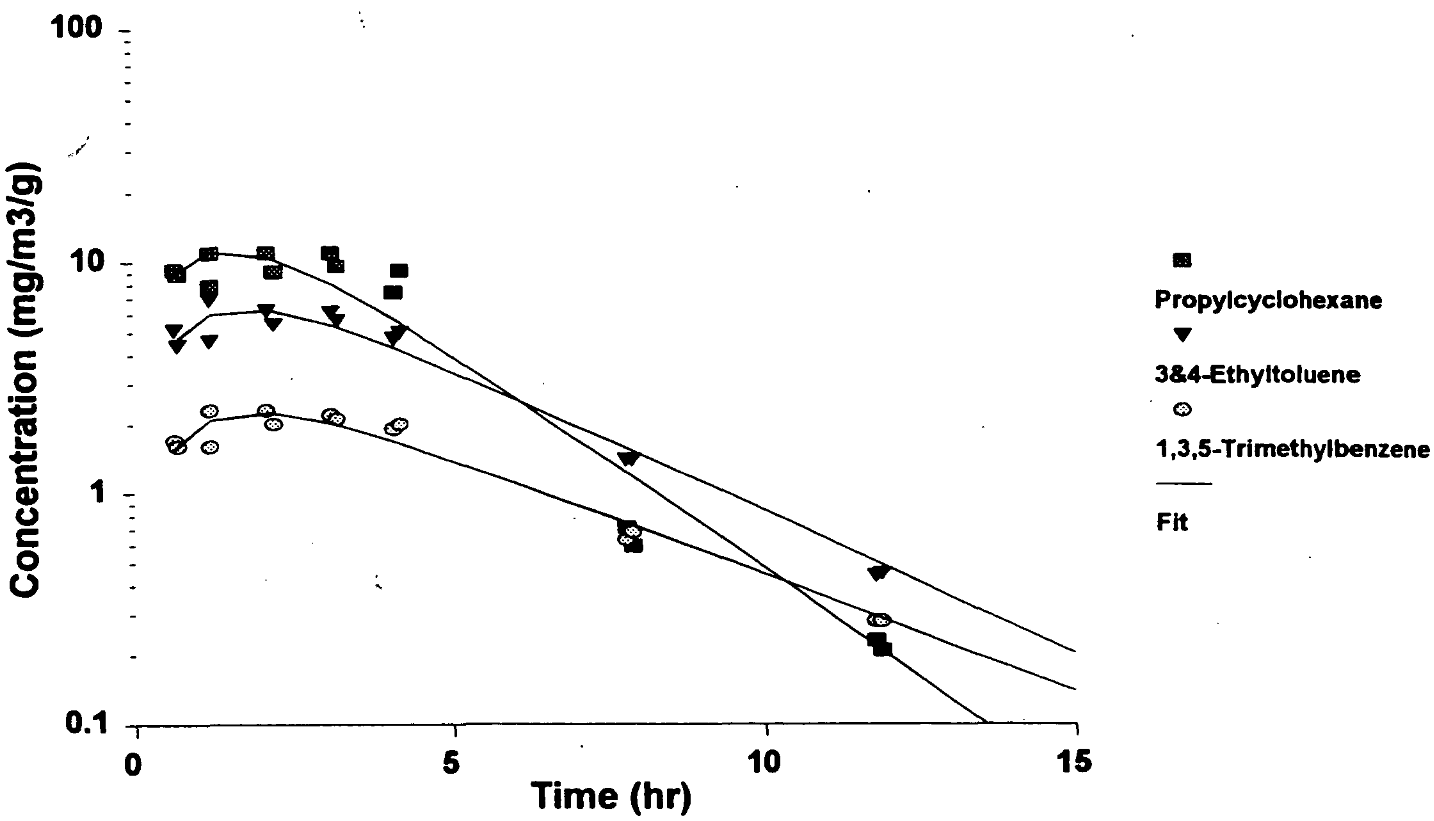
cu m	ACH				
		1			
2-Methyldec	trans-Decah	n-Undecane	Pentylcycloh	n-Dodecane	TVOC
2.1	3.5	6.2	0.38	0.53	589
3.1	5.5	11	0.82	0.94	817
3.7	5.7	12	0.93	1.2	768
4.4	6	14.9	1	1.4	764
4.3	5.4	15	1	1.6	625
1.8	2.1	8.2	1.2	1.7	205
1.3	1.4	7.8	1	2	139
0.091	0.035	1.5	0.17	1.7	18.5
2	3.5	6.1	0.38	0.49	503
2.2	3.7	6.8	0.44	0.62	538
3.7	5.3	13	0.81	1.3	677
3.1	4.9	10.5	0.66	1	671
4.6	6.2	15	1.1	1.5	662
1.6	2.1	9.3	1.2	1.9	203
1.6	1.6	9.3	1.1	2.4	148
0.083	0.033	1.5	0.17	1.8	18.5
1.357	1.303	2.452	1.125	0.953	12.958
0.082	0.058	0.045	0.260	0.110	0.005
2.597E-01	4.282E-01	8.024E-01	5.540E-02	6.950E-02	6.048E+01
1.350E-01	1.804E-01	7.637E-02	4.609E-02	-1.995E-02	2.174E-01
0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	2.457E-05
1.92	2.37	10.51	1.20	1.67	278.16

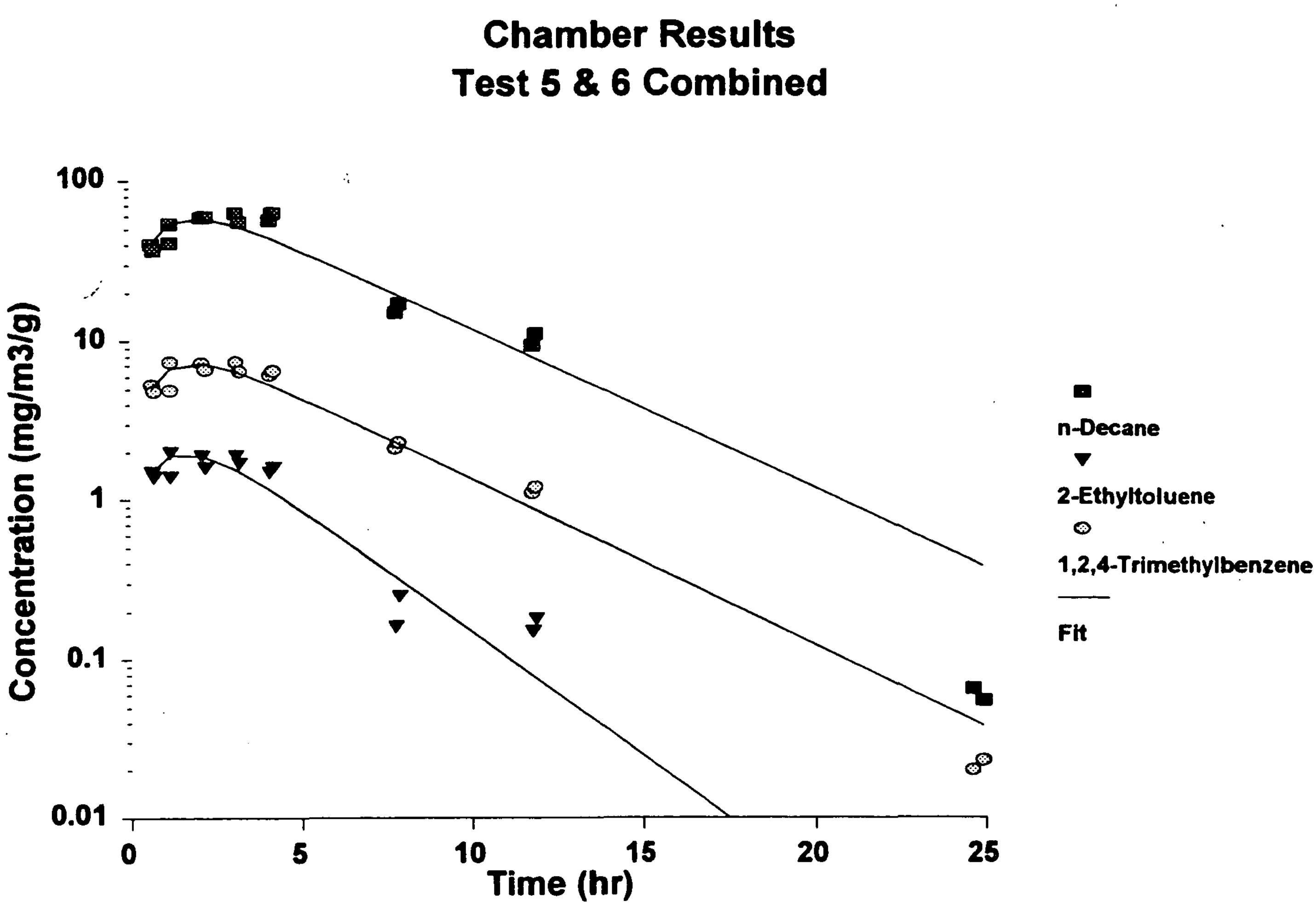
this is total emissions over 24 hrs.
clearly it would be greater, but
we have no way of knowing
how much greater.

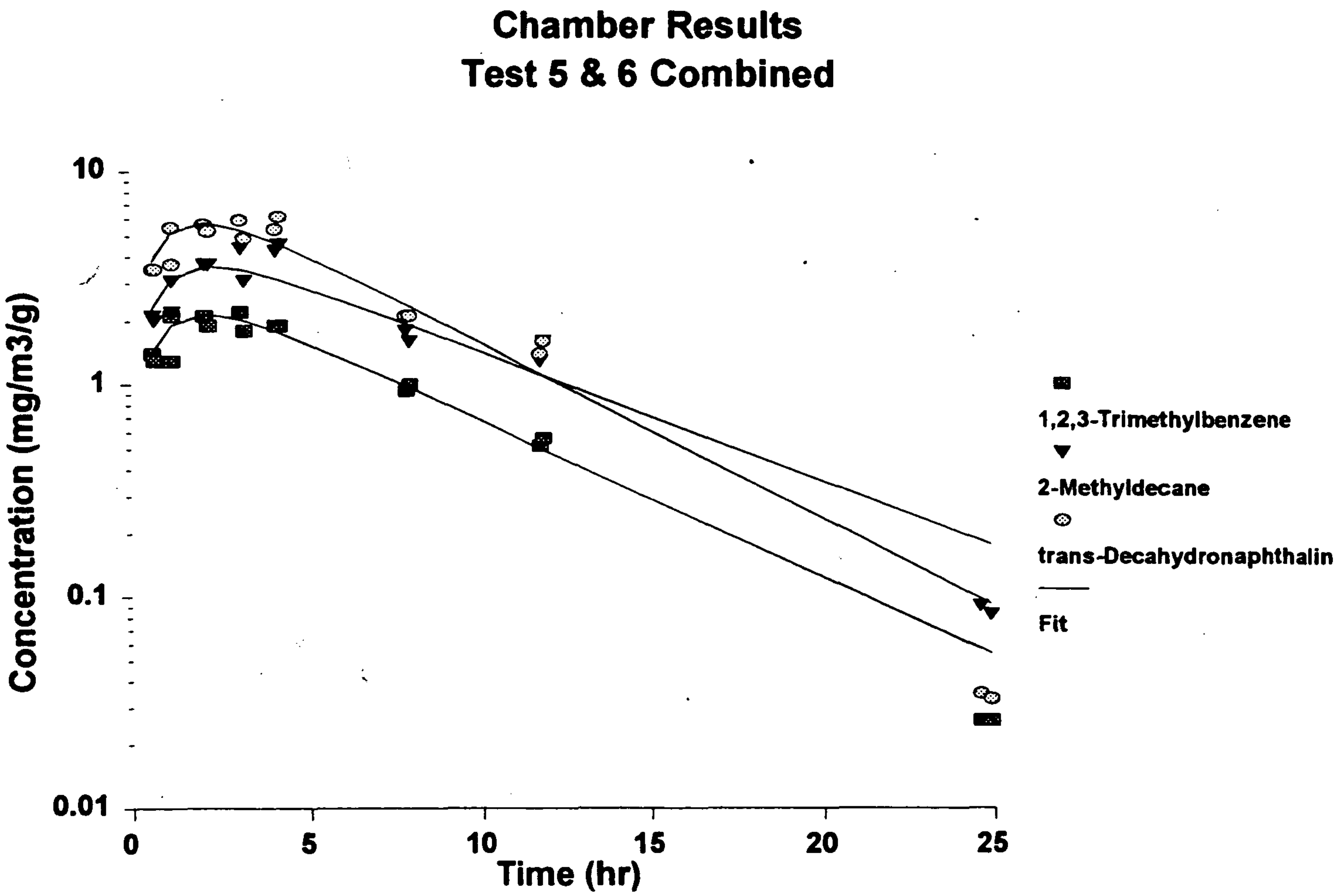


Chamber Results
Test 5 & 6 Combined
Concentration (mg/m3/g)
100
10
1
0.1
0.01
0
5
10
15
Time (hr)
m,p-Xylene
n-Nonane
o-Xylene
Fit

Chamber Results
Test 5 & 6 Combined

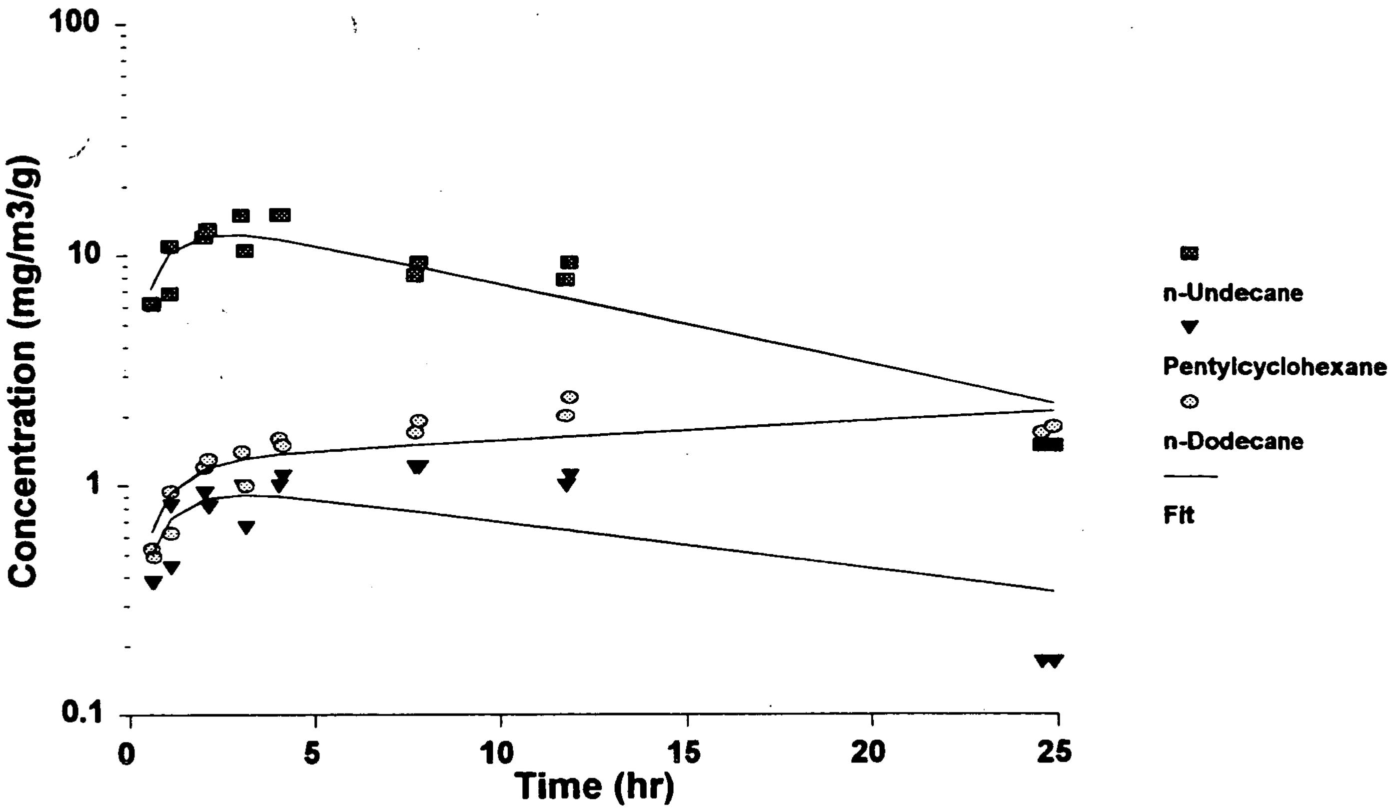


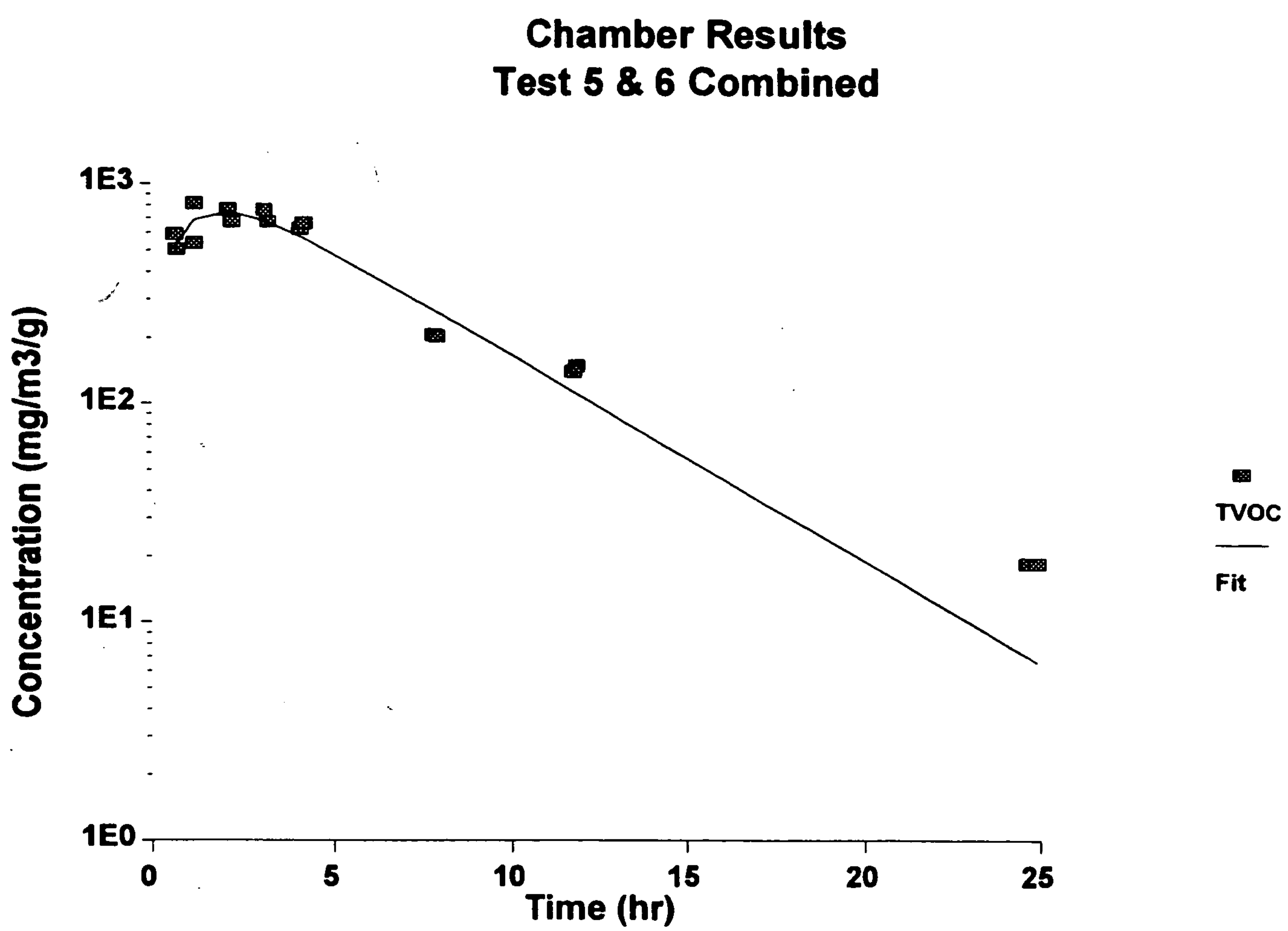

Chamber Results
Test 5 & 6 Combined
Concentration (mg/m3/g)
100
10
1
0.1
0.01
0
5
10
15
20
25
Time (hr)
n-Decane
2-Ethyltoluene
1,2,4-Trimethylbenzene
Fit



Chamber Results
Test 5 & 6 Combined
10
1
0.1
0.01
Concentration (mg/m3/g)
0
5
10
15
20
25
Time (hr)
1,2,3-Trimethylbenzene
2-Methyldecane
trans-Decahydronaphthalin
Fit

Chamber Results
Test 5 & 6 Combined




Chamber Results
Test 5 & 6 Combined
Concentration (mg/m3/g)
1E3
1E2
1E1
1E0
0
5
10
15
20
25
Time (hr)
TVOC
Fit

Chamber VOC Paint Study Vol 0.05276

TEST 11 & 12 Combined

Time hr	m,p-Xylene	n-Nonane	o-Xylene	Propylcycloh	3&4-Ethyltol	1,3,5-Trimet	n-Decane	2-Ethyltoluen	1,2,4-Trimet	1,2,3-Trimet
0.63	5.8	2.7	1.5	0.71	0.52	0.18	8.1	0.17	0.52	0.16
1.1	5	2.3	1.2	0.63	0.5	0.18	7.8	0.16	0.53	0.16
2.1	2.9	1.8	0.81	0.47	0.41	0.15	7.2	0.14	0.49	0.15
3.1	2.1	1.5	0.53	0.37	0.32	0.13	7	0.11	0.41	0.13
4.1	1.3	1.1	0.37	0.31	0.27	0.11	5.9	0.1	0.36	0.12
8.7	0.14	0.24	0.052	0.076	0.092	0.047	2	0.038	0.16	0.059
12.7	0.015	0.062	0.0074	0.021	0.031	0.019	1.5	0.014	0.072	0.031
24.7						0.00081	0.38		0.0043	0.0041
0.63	5	1.9	1.4	0.5	0.43	0.14	5.8	0.13	0.4	0.12
1.1	4.9	2	1.1	0.47	0.4	0.13	5.3	0.13	0.42	0.13
2.1	3.3	1.6	0.83	0.43	0.36	0.13	5.8	0.11	0.37	0.12
3.1	2	1.2	0.56	0.35	0.28	0.1	4.9	0.1	0.31	0.1
4.1	1.3	0.95	0.37	0.24	0.23	0.085	4.3	0.079	0.25	0.082
8.7	0.28	0.41	0.11	0.13	0.13	0.053	1.8	0.046	0.17	0.058
12.7	0.057	0.2	0.027	0.058	0.067	0.035	1.5	0.026	0.11	0.042
24.7	0.00051	0.009	0.0007	0.0037	0.0072	0.0061	0.85	0.0046	0.028	0.015
Sumsq	0.4582	0.5829	0.2171	0.3249	0.2293	0.1878	1.6128	0.1445	0.3417	0.1815
Std	0.026	0.084	0.045	0.188	0.154	0.347	0.062	0.298	0.193	0.336
S0	0.259	0.123	0.057	0.031	0.024	0.009	0.395	0.008	0.027	0.008
K	0.462	0.274	0.379	0.247	0.199	0.177	0.145	0.174	0.162	0.130
C0	6.688	2.371	1.839	0.628	0.515	0.154	6.250	0.155	0.439	0.135
Emission (mg/g)	1.32	0.90	0.41	0.26	0.26	0.10	4.98	0.09	0.31	0.12

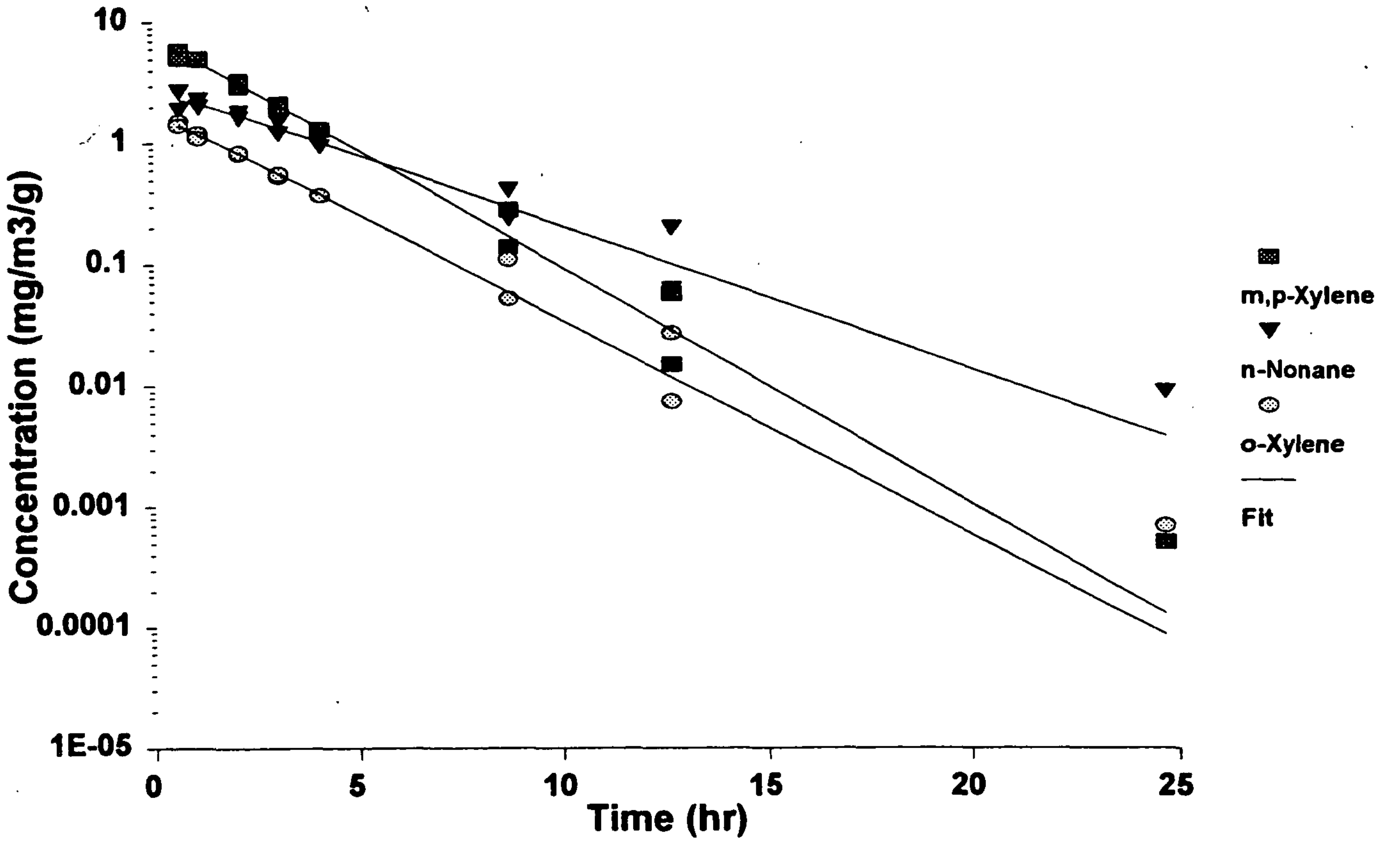
$S(t) = S0 \exp(-kt)$ with C0 = Concentration at t=0

cu m ACH

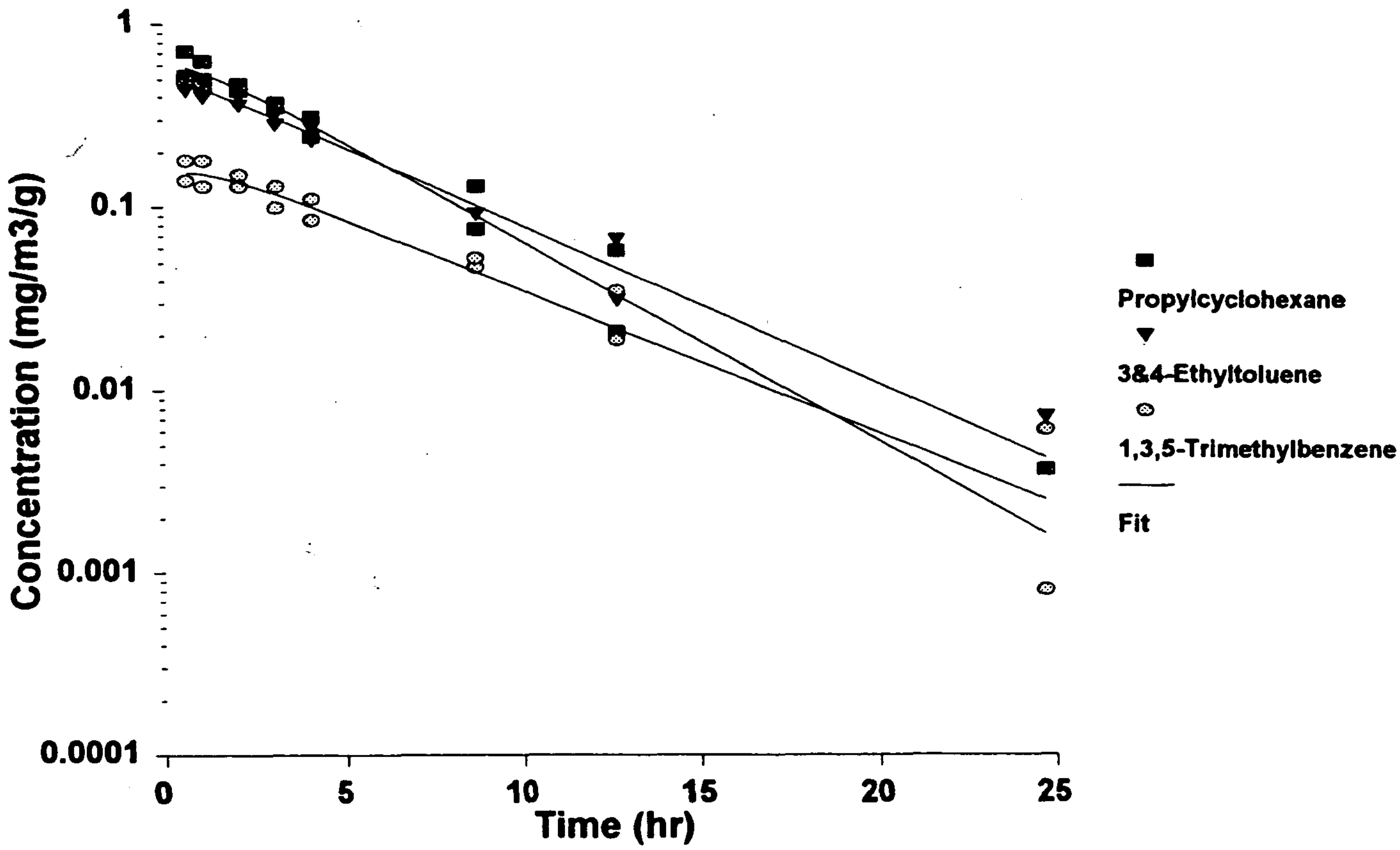
1

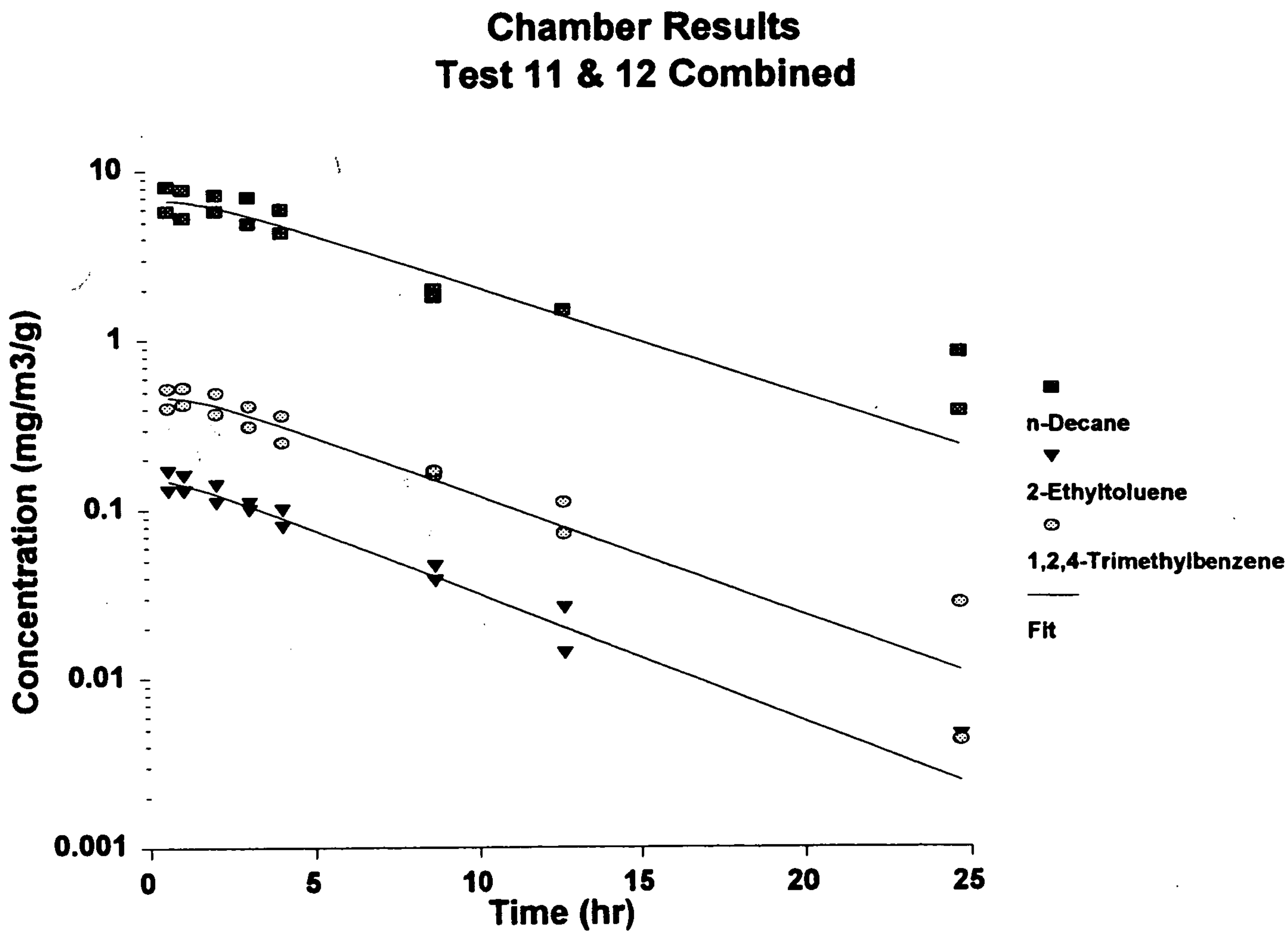
2-Methyldec	trans-Decah	n-Undecane	Pentylcycloh	n-Dodecane	TVOC
3	4.5	13.3	2	2.3	240
3.3	4.9	13.5	2.3	2.8	270
3.3	4.9	13.5	2.1	2.8	250
3.2	4.4	13.7	2	3	240
3.2	4.4	13.8	2.4	3.2	220
0.81	1.3	2.7	0.64	1.3	100
0.79	1.1	2.1	0.62	1.3	89
0.93	0.39	2.7	0.69	1.8	62
2.1	3.6	10.3	1.2	1.7	160
2.3	4	10.8	1.6	2	170
2.4	3.6	10.8	1.7	2.1	170
2	3.1	9.8	1.4	1.9	140
1.9	2.7	9.6	1.3	1.6	120
0.81	1.3	1.9	0.58	1.1	71
0.73	1.2	1.8	0.59	1	68
0.82	0.82	1.8	0.52	1.1	53
1.6552	1.3985	3.0289	1.3706	1.5465	12.8174
0.139	0.079	0.061	0.158	0.134	0.014
0.168	0.249	0.992	0.109	0.117	10.007
0.127	0.128	0.231	0.106	0.039	0.070
2.117	3.880	5.644	1.283	2.098	224.077
2.20	3.54	5.58	1.68	5.85	311.82

Chamber Results
Test 11 & 12 Combined



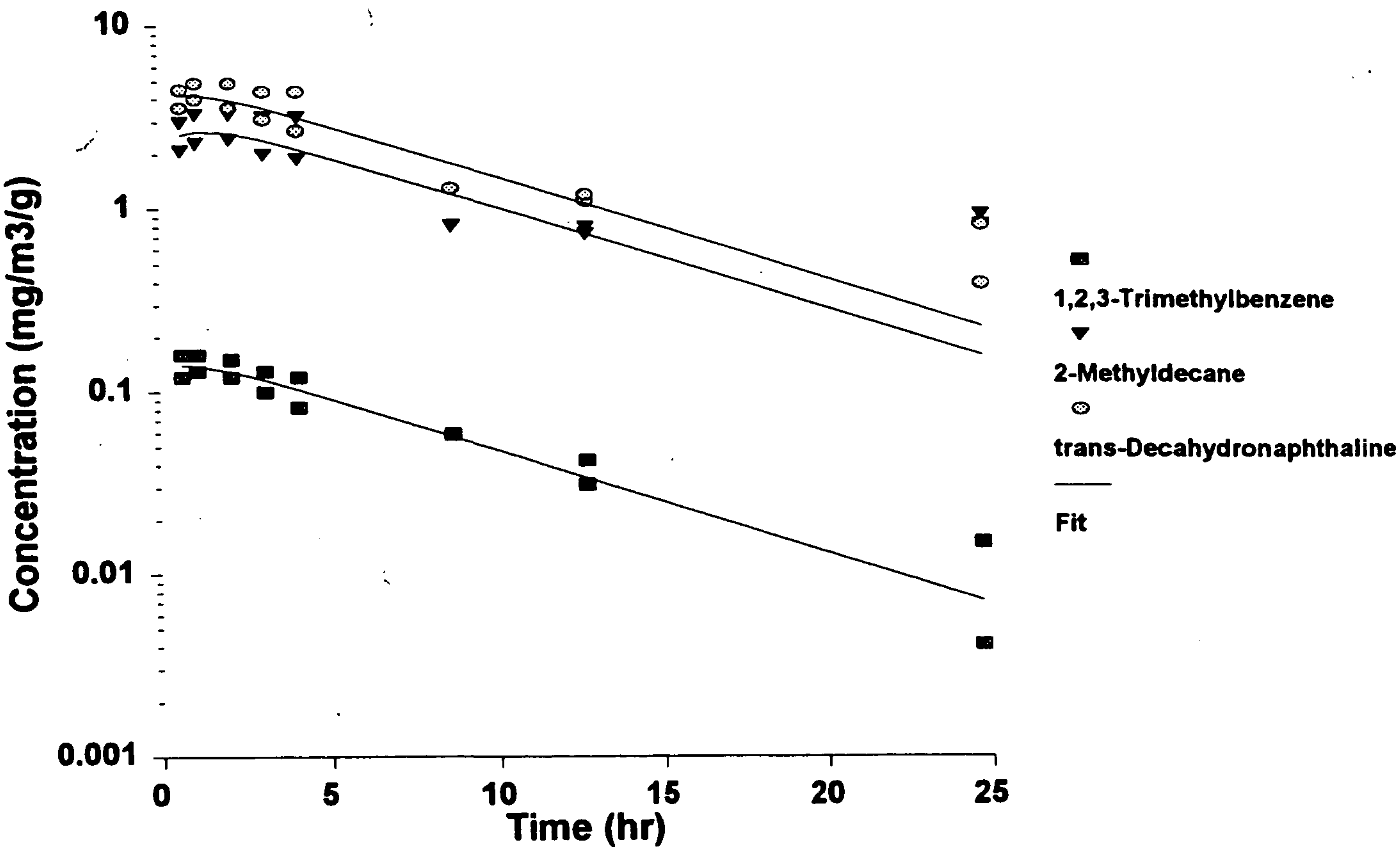
Chamber Results
Test 11 & 12 Combined



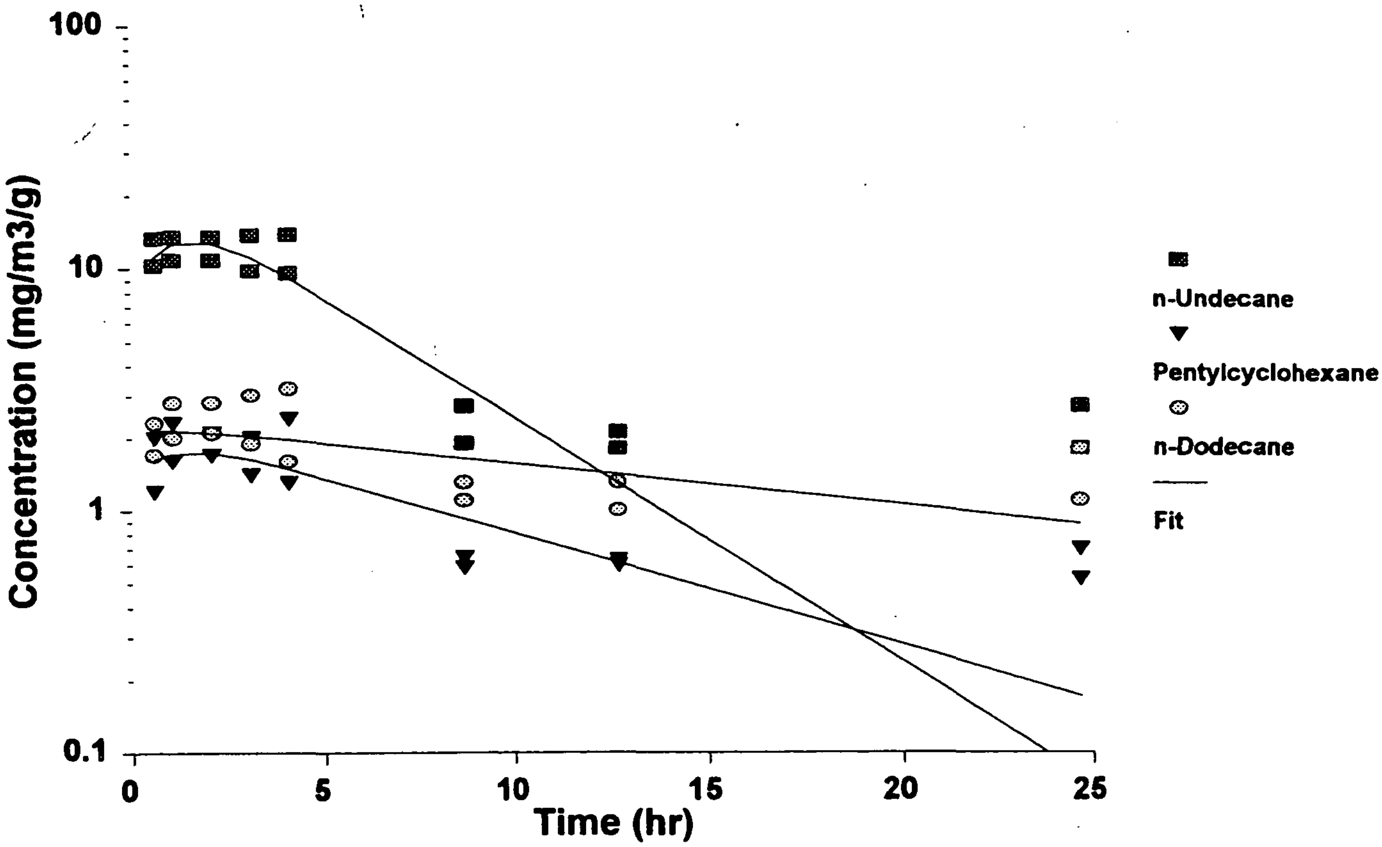


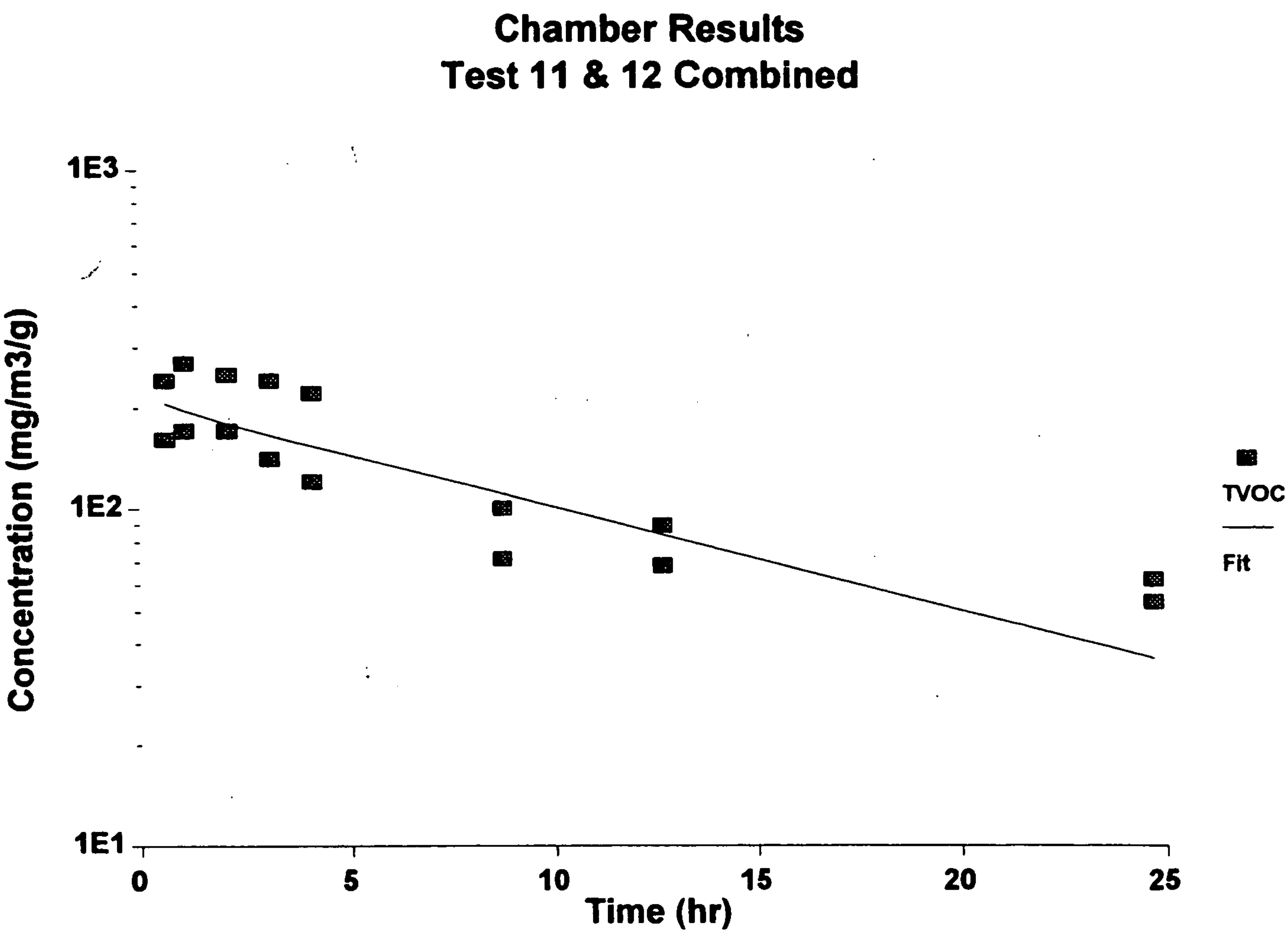
Chamber Results
Test 11 & 12 Combined
Concentration (mg/m3/g)
10
1
0.1
0.01
0.001
0
5
10
15
20
25
Time (hr)
n-Decane
2-Ethyltoluene
1,2,4-Trimethylbenzene
Fit

Chamber Results
Test 11 & 12 Combined



Chamber Results
Test 11 & 12 Combined





Chamber Results
Test 11 & 12 Combined
1E3
1E2
1E1
Concentration (mg/m3/g)
0
5
10
15
20
25
Time (hr)
TVOC
Fit

Chamber VOC Recovery Study Vol 0.05276

TEST 13 & 14 Combined

Time hr	m,p-Xylene	n-Nonane	o-Xylene	Propylcycloh	3&4-Ethyltol	1,3,5-Trimet	n-Decane	2-Ethyltoluen	1,2,4-Trimet	1,2,3-Trimet
0.65	9.1	11.4	2.8	2.8	2.4	0.82	11.8	0.78	2.4	0.67
1.2	10	12.4	2.9	2.9	2.8	1	13.6	0.89	2.7	0.8
2.1	8.3	11	2.5	3	2.8	0.94	13.6	0.9	2.8	0.86
3.1	6	10.5	2	2.8	2.7	1	13.5	0.9	2.8	0.87
4.1	4.3	8.2	1.5	2.1	2.3	0.8	12.3	0.77	2.5	0.76
7.8	0.82	2.24	0.4	0.52	1.08	0.39	3.03	0.22	1.12	0.48
11.8	0.16	0.97	0.09	0.34	0.62	0.28	3.05	0.19	0.9	0.39
24.8					0.037	0.035	1.6	0.025	0.177	0.11
0.7	9.2	10.6	2.8	2.5	2.1	0.69	12.9	0.67	2	0.54
1.2	10.6	12.6	3.3	3.1	2.7	0.87	14.4	0.85	2.6	0.72
2.2	9	12.1	2.7	2.9	2.7	0.89	14.8	0.85	2.6	0.77
3.2	6.8	10.7	2	2.6	2.4	0.85	14.5	0.83	2.4	0.72
4.2	5.4	9.8	1.6	2.4	2.3	0.76	13.2	0.73	2.3	0.68
7.9	1.3	2.94	0.57	0.7	1.22	0.41	3.18	0.28	1.19	0.49
11.9	0.38	1.54	0.2	0.45	0.88	0.34	3.19	0.24	1.03	0.44
24.9		0.08	0.006	0.034	0.14	0.093	2.1	0.074	0.39	0.19
Sumsq	0.7714	1.0457	0.3815	0.6164	0.4705	0.3436	2.6649	0.4621	0.6482	0.3053
~~Sumsq/S0~~ Std	0.022	0.024	0.033	0.057	0.047	0.095	0.050	0.142	0.064	0.097
S0	8.663E-01	1.022E+00	2.266E-01	2.565E-01	2.028E-01	6.430E-02	1.200E+00	6.813E-02	1.786E-01	5.047E-02
K	4.183E-01	2.773E-01	3.351E-01	2.741E-01	1.682E-01	1.397E-01	2.355E-01	1.971E-01	1.246E-01	8.314E-02
C0	4.631E+00	4.555E+00	1.949E+00	8.834E-01	9.780E-01	3.976E-01	3.525E+00	2.678E-01	1.301E+00	3.219E-01

S(t) = S0 exp(-kt) with C0 = Concentration at t=0

Emission (mg/g)	2.66	4.55	0.98	1.11	1.51	0.61	5.88	0.42	1.98	0.81

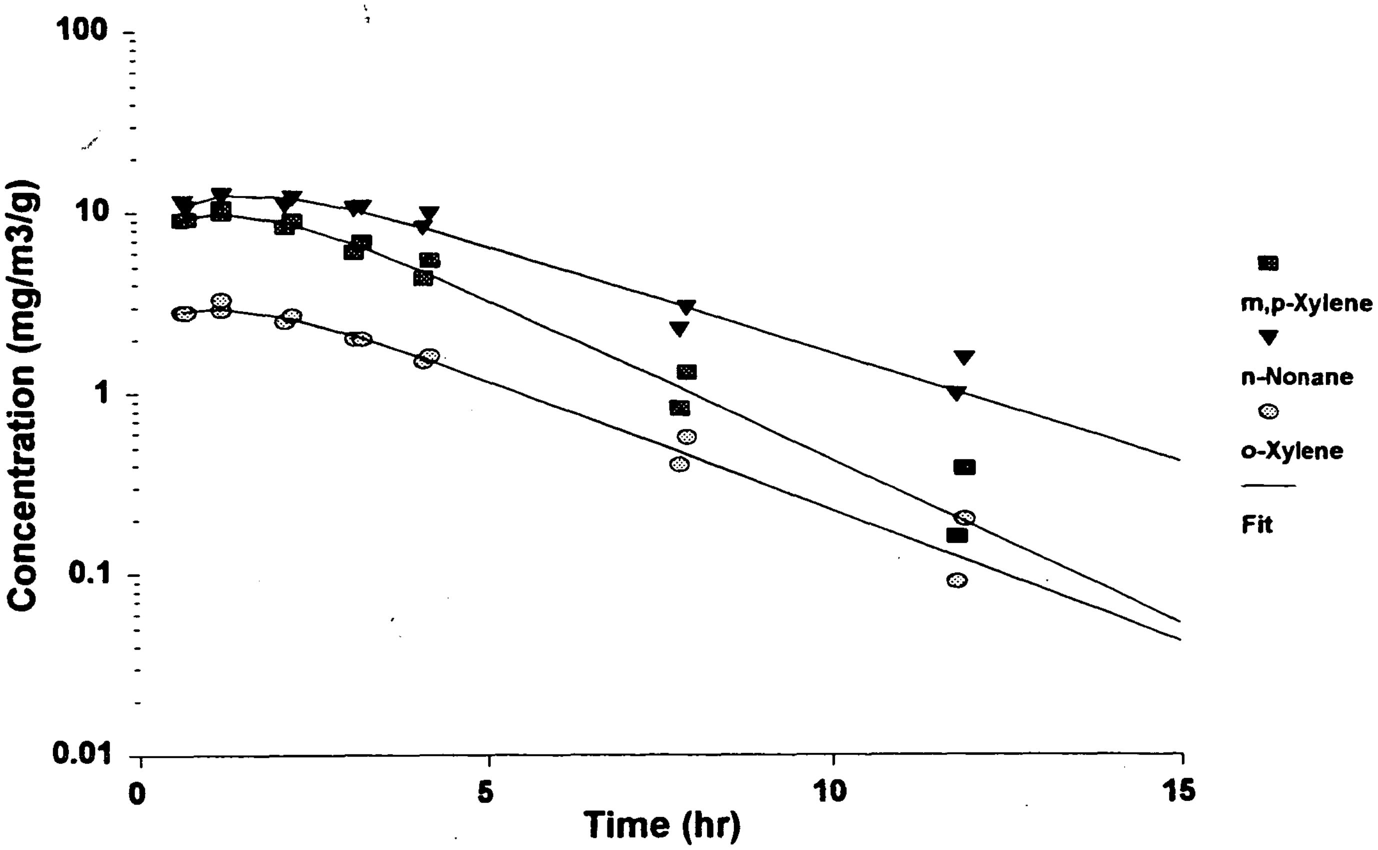
cu m ACH

1

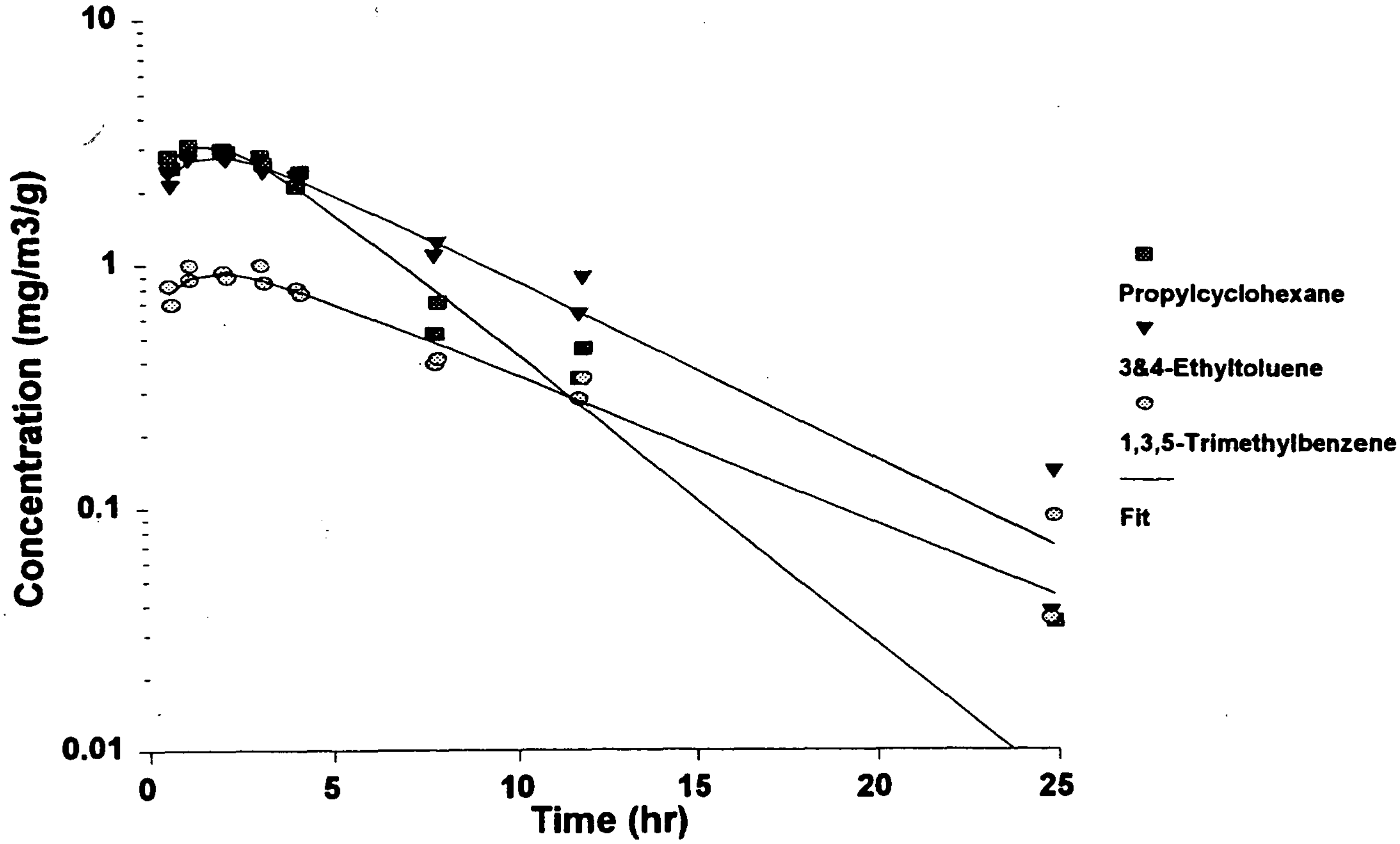
2-Methyldec	trans-Decah	n-Undecane	Pentylcycloh	n-Dodecane	TVOC
1.4	2	6.5	0.64	0.89	200.9
1.9	2.7	8.5	0.87	1.2	240
2	2.9	8.4	0.94	1.4	240
2.4	3.2	9.4	1	1.5	240
2.2	2.9	9.1	0.95	1.5	220
1.01	1.47	2.17	0.63	1.19	103
1.06	1.43	2.26	0.75	1.42	95
1	0.639	2.5	0.59	1.7	55
1.2	1.9	6.4	0.68	0.77	170
1.7	2.6	8.4	0.83	1	200
1.8	2.7	9.2	0.83	1.2	202
1.9	2.6	8.6	0.81	1.2	190
1.7	2.5	8.1	0.84	1.2	160
1.04	1.52	2.35	0.68	1.12	89
1.07	1.51	2.48	0.65	1.36	66
0.94	0.88	2.1	0.5	1.2	45
1.0036	0.7867	2.6110	0.3592	0.5341	9.2442
0.116	0.068	0.077	0.100	0.087	0.011
1.061E-01	1.704E-01	7.384E-01	4.913E-02	6.965E-02	1.279E+01
4.594E-02	7.291E-02	2.079E-01	2.586E-02	-1.718E-03	9.594E-02
8.669E-01	1.033E+00	1.237E-01	4.828E-01	4.163E-01	1.580E+02
3.31	3.08	3.58	2.89	1.67	220.19

>

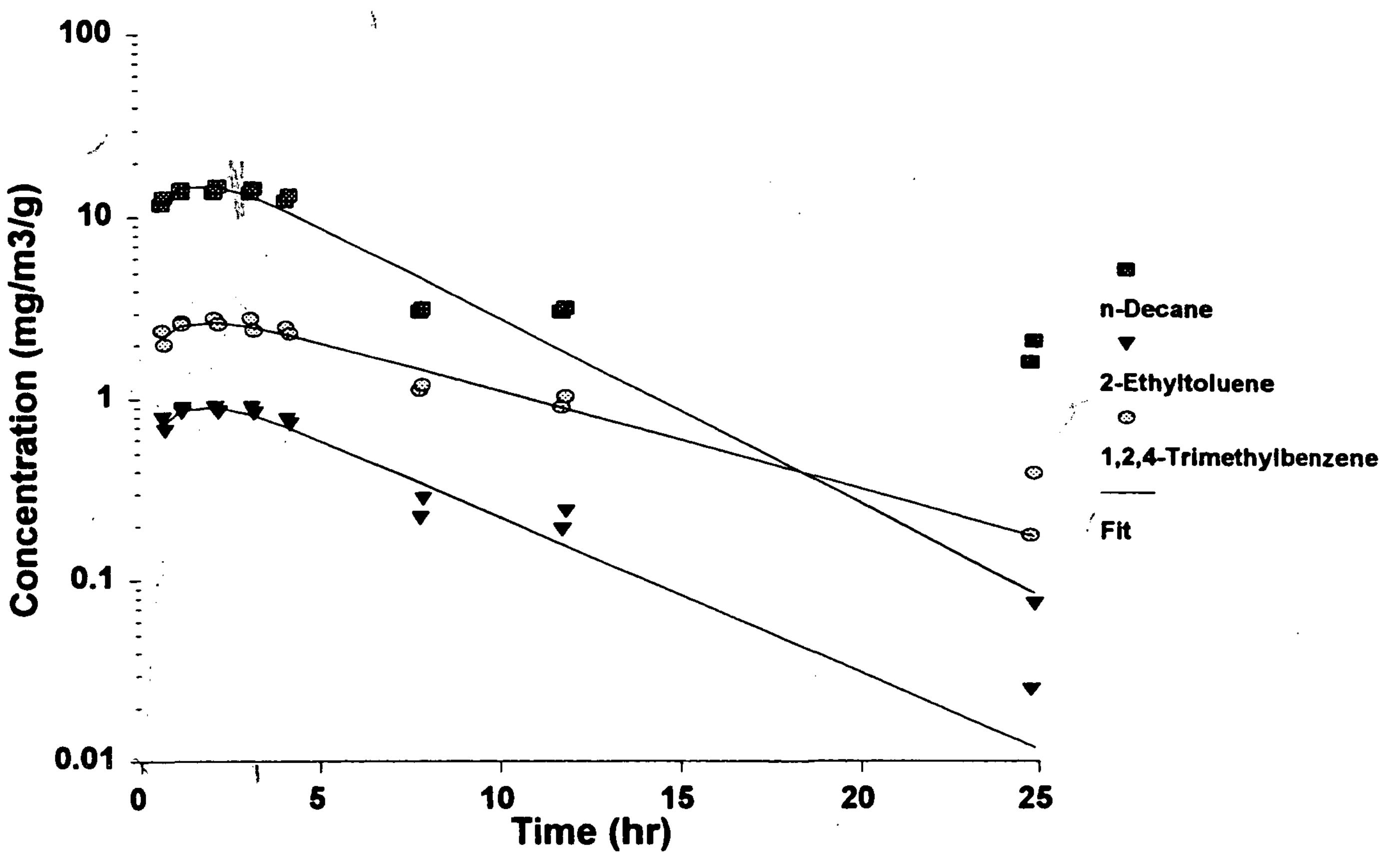
Chamber Results
Test 13 & 14 Combined



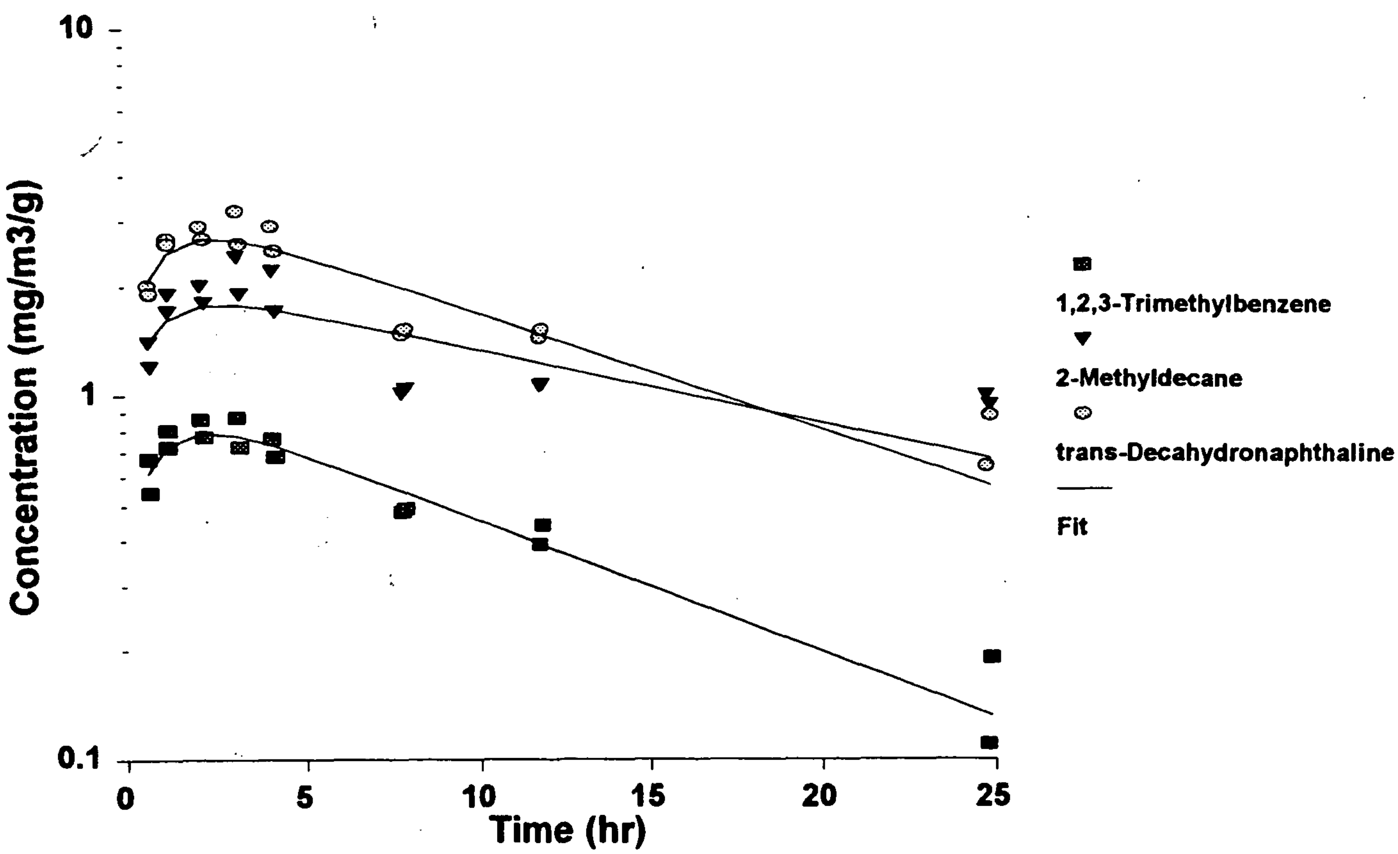
Chamber Results
Test 13 & 14 Combined

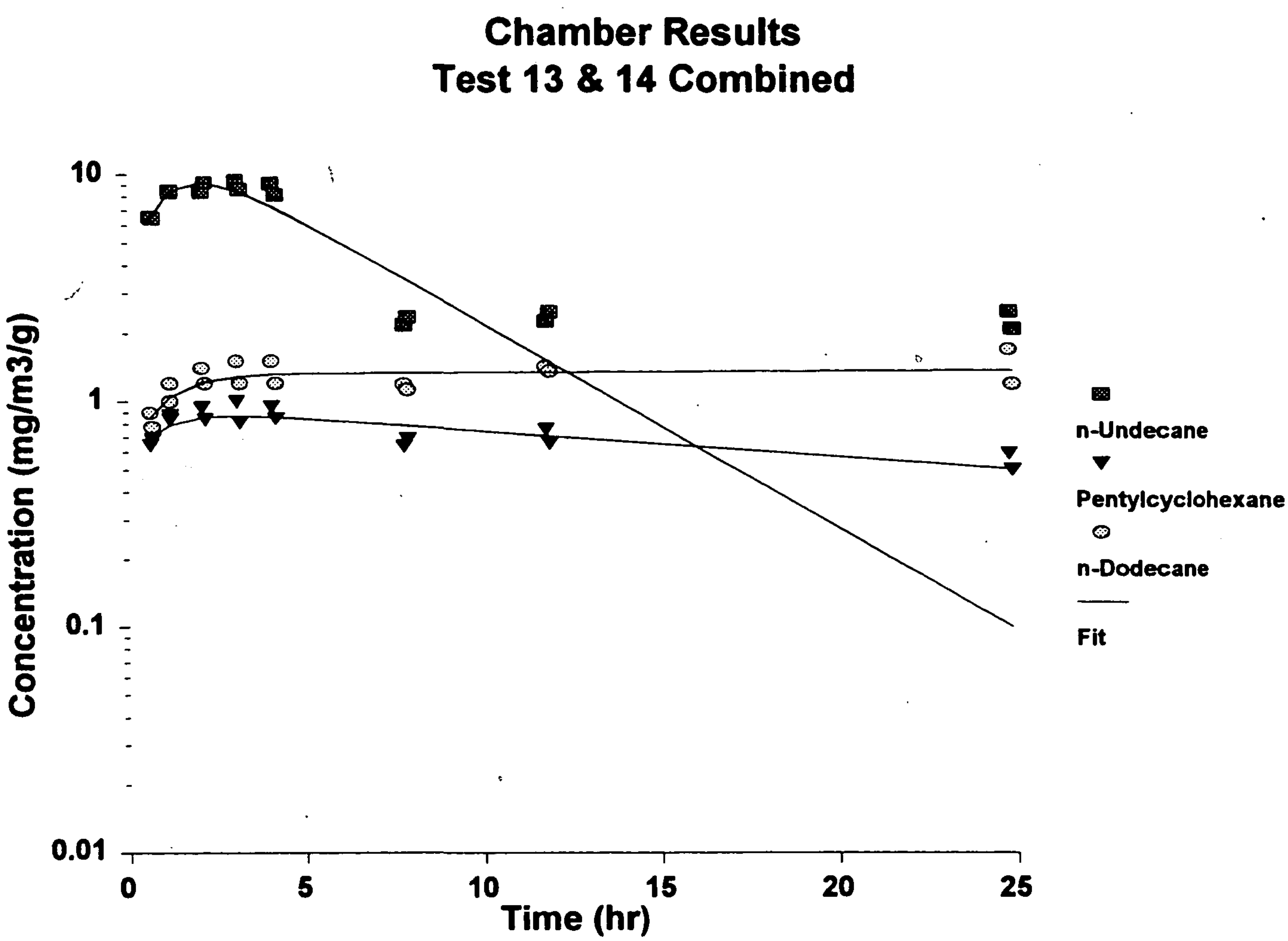


Chamber Results
Test 13 & 14 Combined

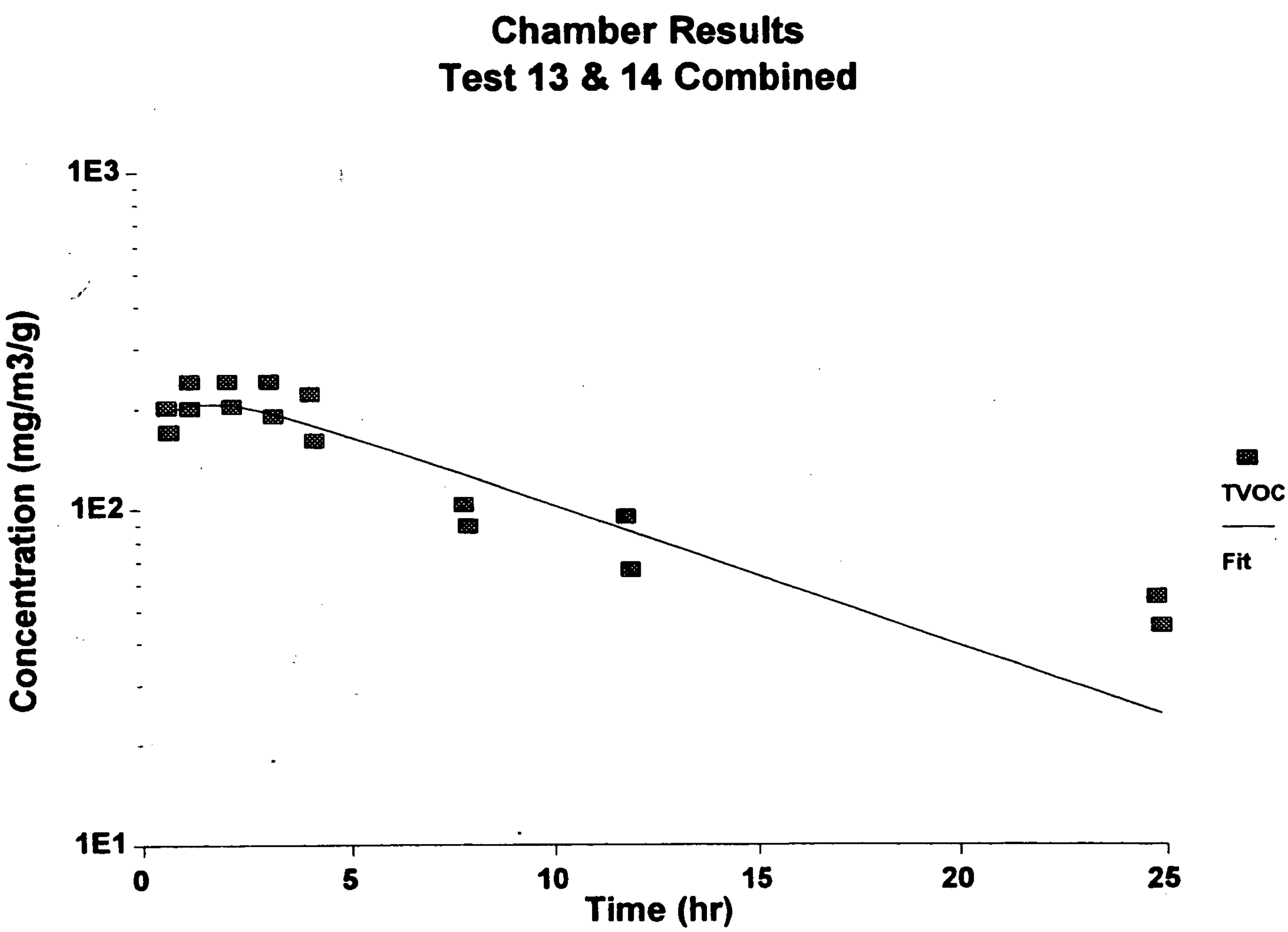


Chamber Results
Test 13 & 14 Combined





Chamber Results
Test 13 & 14 Combined
10
1
0.1
0.01
Concentration (mg/m3/g)
0
5
10
15
20
25
Time (hr)
n-Undecane
Pentylcyclohexane
n-Dodecane
Fit



Chamber Results
Test 13 & 14 Combined
1E3
1E2
1E1
Concentration (mg/m3/g)
0
5
10
15
20
25
Time (hr)
TVOC
Fit

Chamber	VOC	Recovery	Study	TEST 21 & 22 w & w/o fan					Vol	0.05276
	w Fan	w/o Fan								
Time	m,p-Xylene	n-Nonane	o-Xylene	Propylcycloh	3&4-Ethyltol	1,3,5-Trimet	n-Decane	2-Ethyltoluen	1,2,4-Trimet	1,2,3-Trimet
hr	7.09									
0.67	19.75	59.24	3.53	16.93	1.41	0.42	76.16	0.39	1.69	0.42
1.2	16.93	57.83	3.53	16.93	1.21	0.65	76.16	0.38	1.69	0.42
2.2	9.59	39.49	1.97	11.28	0.96	0.59	80.39	0.28	1.55	0.44
3.2	5.64	28.21	1.31	8.32	0.78	0.44	70.52	0.25	1.41	0.38
4.2	3.39	17.77	0.76	5.36	0.58	0.35	66.29	0.18	1.07	0.31
8.2	0.20	1.23	0.06	0.47	0.10	0.08	12.55	0.04	0.31	0.12
12.7		0.07		0.03	0.01	0.01	2.96		0.06	0.03
24.7							0.04			
	7.56									
0.67	11.90	27.78	2.12	6.88	0.53	0.22	29.10	0.15	0.62	0.15
1.2	13.49	34.39	2.38	8.99	0.66	0.26	41.01	0.17	0.81	0.19
2.2	10.71	33.07	1.98	9.26	0.66	0.33	39.68	0.17	0.90	0.21
3.2	7.41	27.78	1.46	7.28	0.57	0.29	38.36	0.16	0.87	0.21
4.2	5.29	22.49	1.16	6.22	0.53	0.28	38.36	0.15	0.78	0.19
8.2	0.83	6.22	0.24	1.98	0.26	0.16	14.55	0.08	0.49	0.13
12.7	0.12	1.85	0.04	0.70	0.12	0.09	13.23	0.05	0.32	0.11
24.7							0.62		0.01	0.01
Sumsq	0.2676	0.7316	0.2200	0.4119	0.1452	0.1109	2.3119	0.0723	0.1585	0.0629
Std	0.006	0.005	0.028	0.010	0.042	0.070	0.011	0.082	0.038	0.059
S0	1.137	5.244	0.261	1.427	0.091	0.058	7.821	0.026	0.142	0.035
K	0.693	0.619	0.664	0.577	0.396	0.377	0.328	0.342	0.311	0.248
C0	22.990	39.380	3.395	12.267	1.227	0.000	11.906	0.350	0.894	0.217
Emission	3.39	11.82	0.66	3.59	0.39	0.15	25.73	0.13	0.61	0.19
(mg/g)										
Sumsq	0.2174	0.3021	0.1062	0.2374	0.0539	0.0508	1.9158	0.0143	0.2827	0.1530
Std	0.007	0.004	0.018	0.010	0.033	0.063	0.018	0.034	0.119	0.273
S0	1.177	3.037	0.193	0.786	0.049	0.022	3.198	0.012	0.070	0.015
K	0.480	0.307	0.389	0.278	0.177	0.136	0.173	0.137	0.161	0.121
C0	5.827	5.356	1.167	0.810	0.232	0.042	3.785	0.084	0.000	0.010
Emission	3.09	10.80	0.65	2.98	0.34	0.18	19.63	0.12	0.44	0.13
(mg/g)										

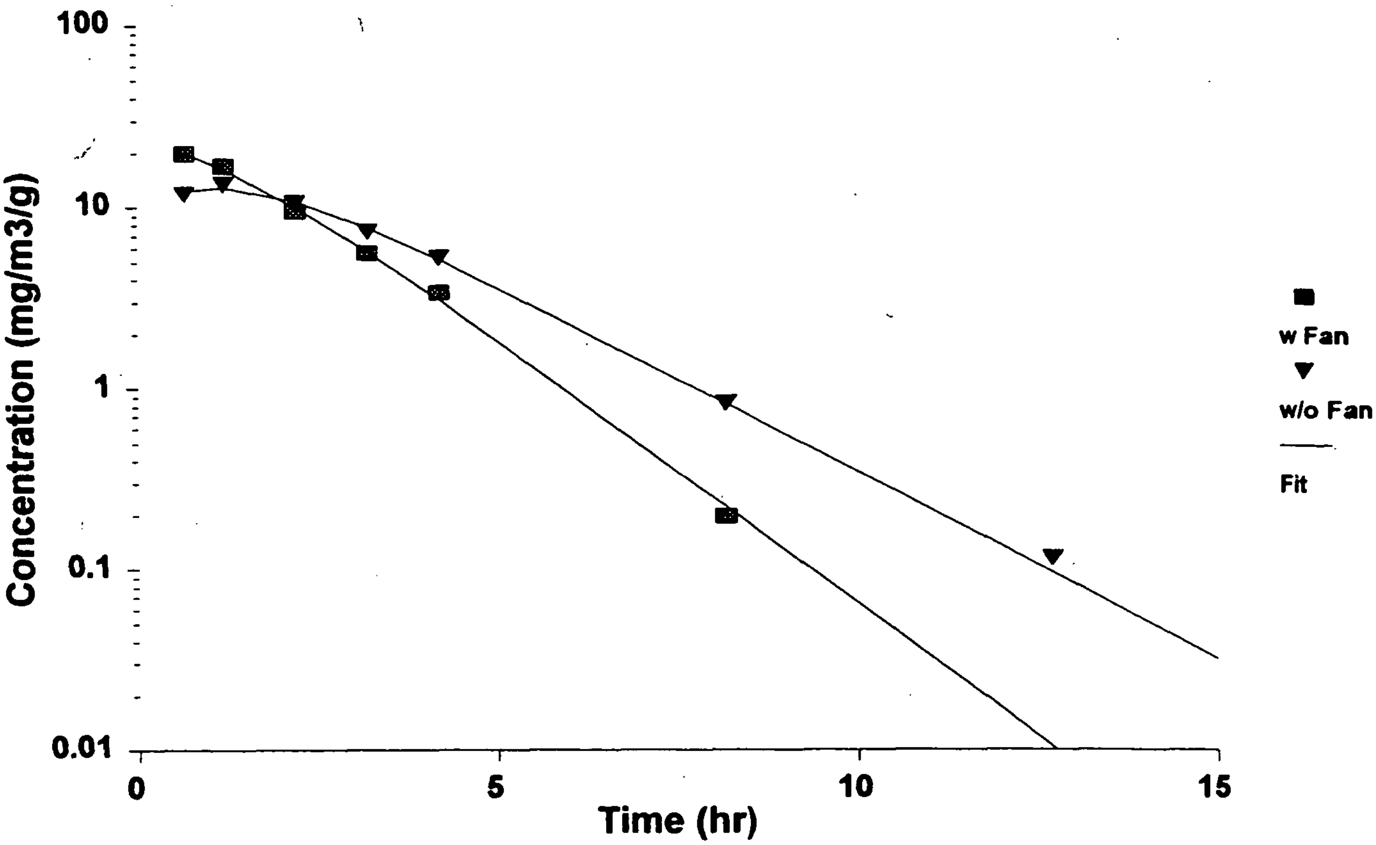
S(t) = S0 exp(-kt) with C0 = Concentration at t=0

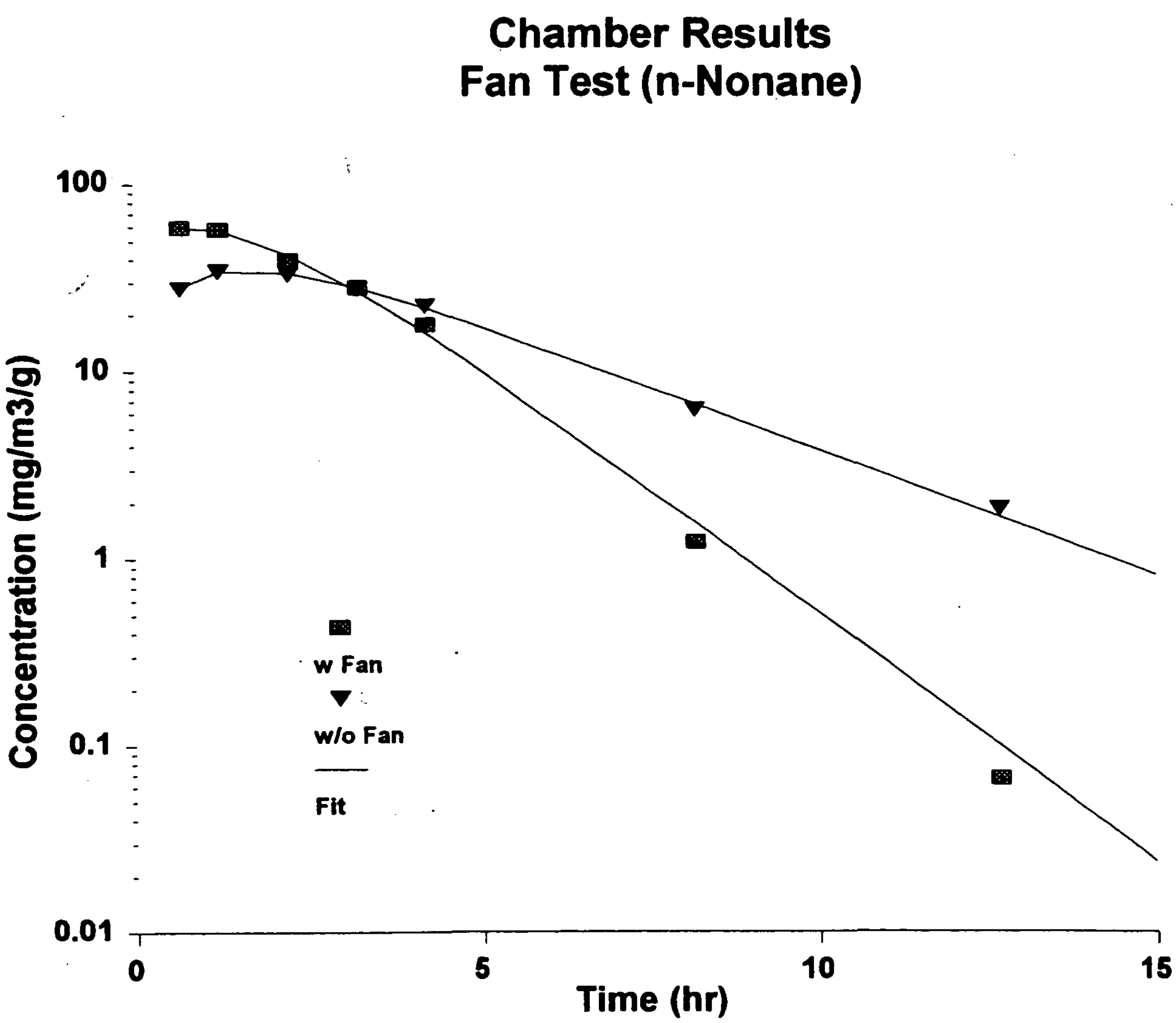
cu m ACH

1

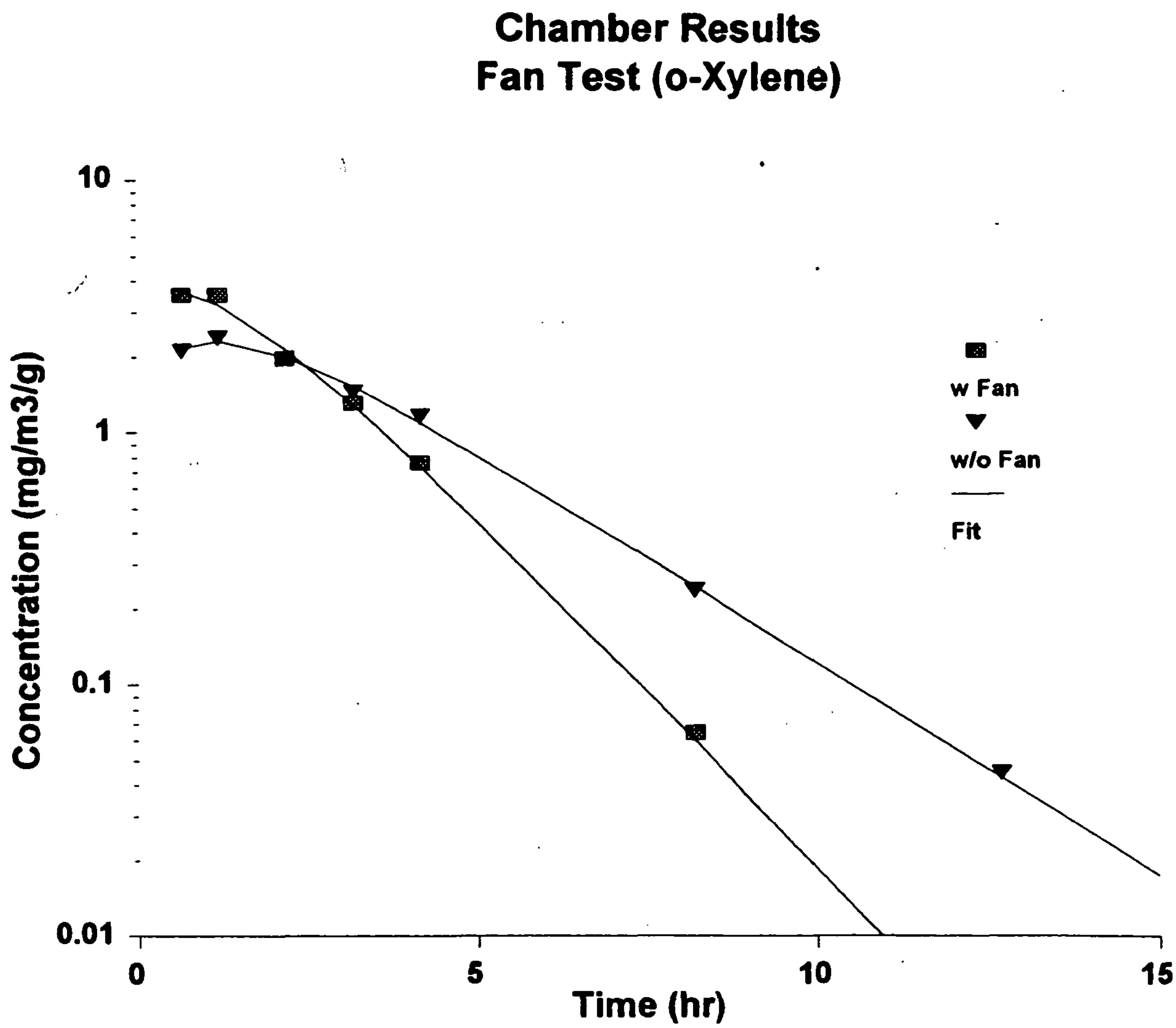
2-Methyldec	trans-Decah	n-Undecane	Pentylcycloh	n-Dodecane	TVOC
7.05	9.87	31.03	2.26	3.81	1086.04
8.04	11.00	38.08	2.40	4.65	1043.72
9.03	10.86	42.31	3.10	5.36	902.68
9.17	10.30	42.31	3.67	6.49	803.95
9.73	8.89	52.19	3.95	7.05	705.22
4.65	3.24	15.51	3.39	8.04	253.88
1.69	0.85	11.00	1.83	7.76	121.30
0.02	0.01	0.38	0.06	1.97	9.59
1.72	3.17	7.94	0.50	0.82	370.37
2.51	4.37	10.71	0.85	1.18	476.19
3.17	4.89	13.10	0.97	1.46	476.19
3.04	4.63	15.74	1.04	1.72	451.19
3.31	4.89	17.20	1.16	1.72	410.05
3.17	3.31	9.79	1.32	2.25	238.10
3.57	2.91	10.98	1.72	3.04	185.19
0.93	0.30	8.86	1.32	6.08	68.78
1.2009	0.5582	2.6503	1.3435	1.6055	3.2797
0.047	0.019	0.019	0.129	0.075	0.001
0.803	0.992	3.583	0.260	0.413	66.556
0.208	0.264	0.185	0.133	0.042	0.210
0.000	2.183	0.000	0.000	0.000	982.508
3.87	4.20	19.39	1.96	9.74	564.20
0.8511	0.7513	1.3244	0.3826	0.0922	3.7837
0.090	0.058	0.029	0.084	0.006	0.003
0.206	0.357	0.841	0.061	0.079	29.839
0.047	0.109	0.030	-0.010	-0.059	0.098
0.000	0.000	0.000	0.000	0.176	240.414
4.34	3.27	28.07	1.46	1.89	433.81
		>	>		

Chamber Results
Fan Test (m,p-Xylene)

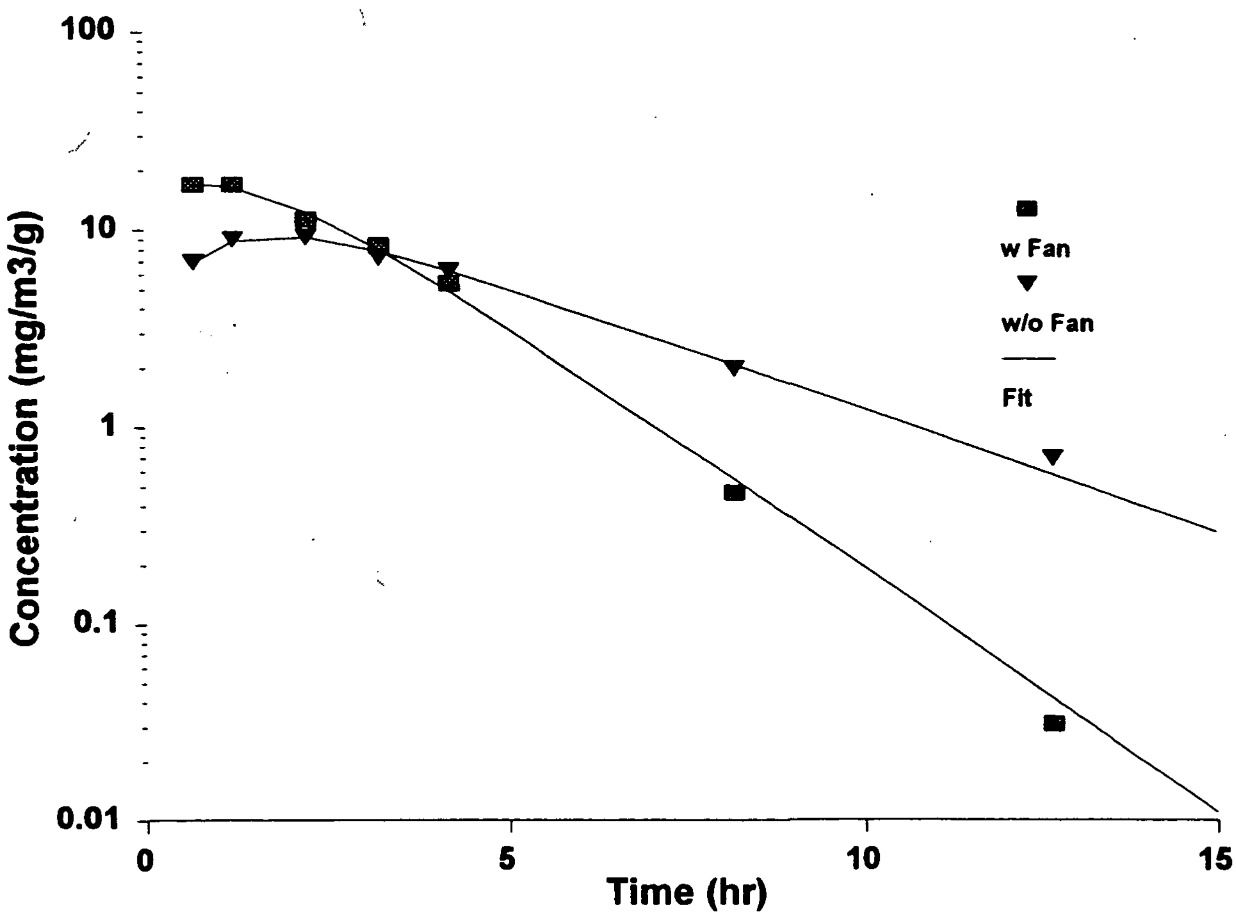




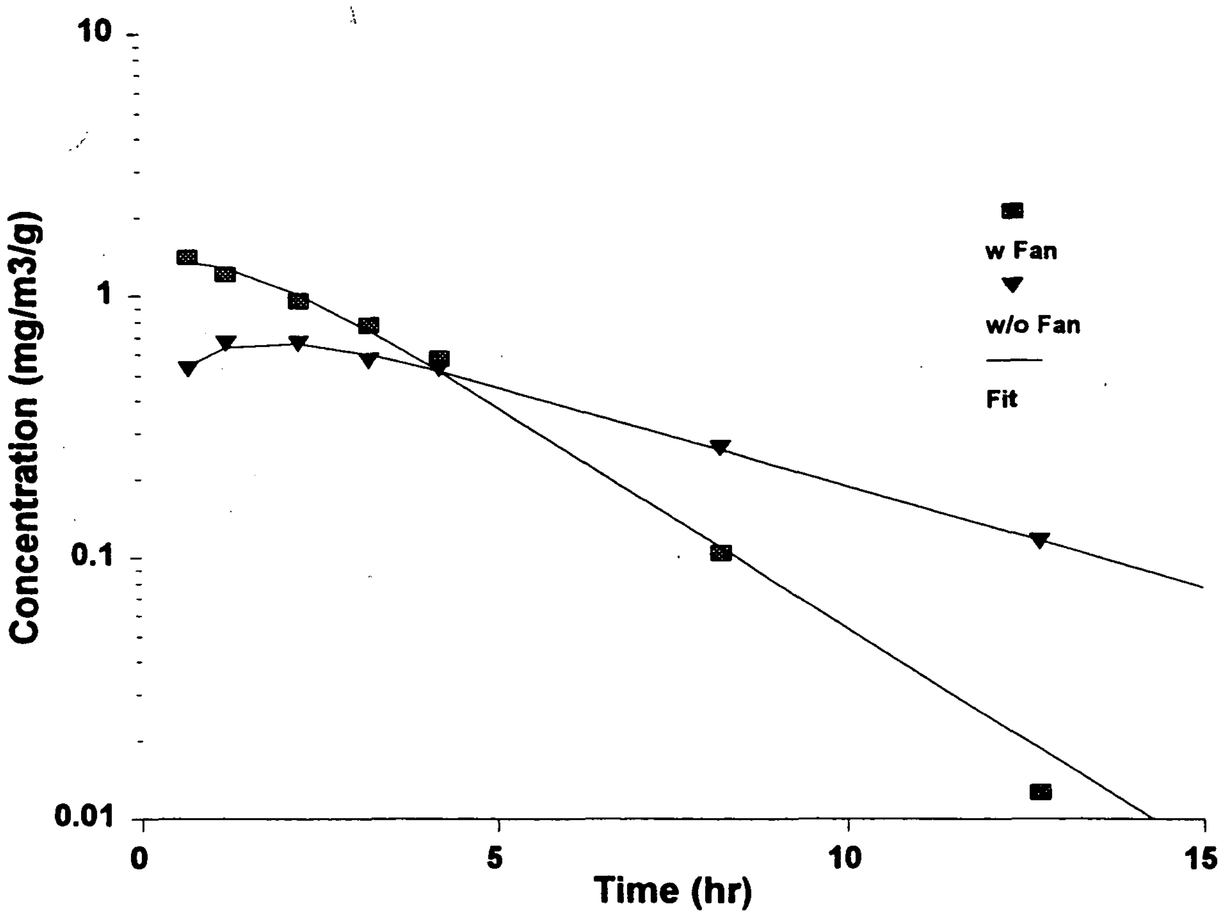
Chamber Results
Fan Test (n-Nonane)
100
10
1
0.1
0.01
Concentration (mg/m3/g)
w Fan
w/o Fan
Fit
0
5
10
15
Time (hr)

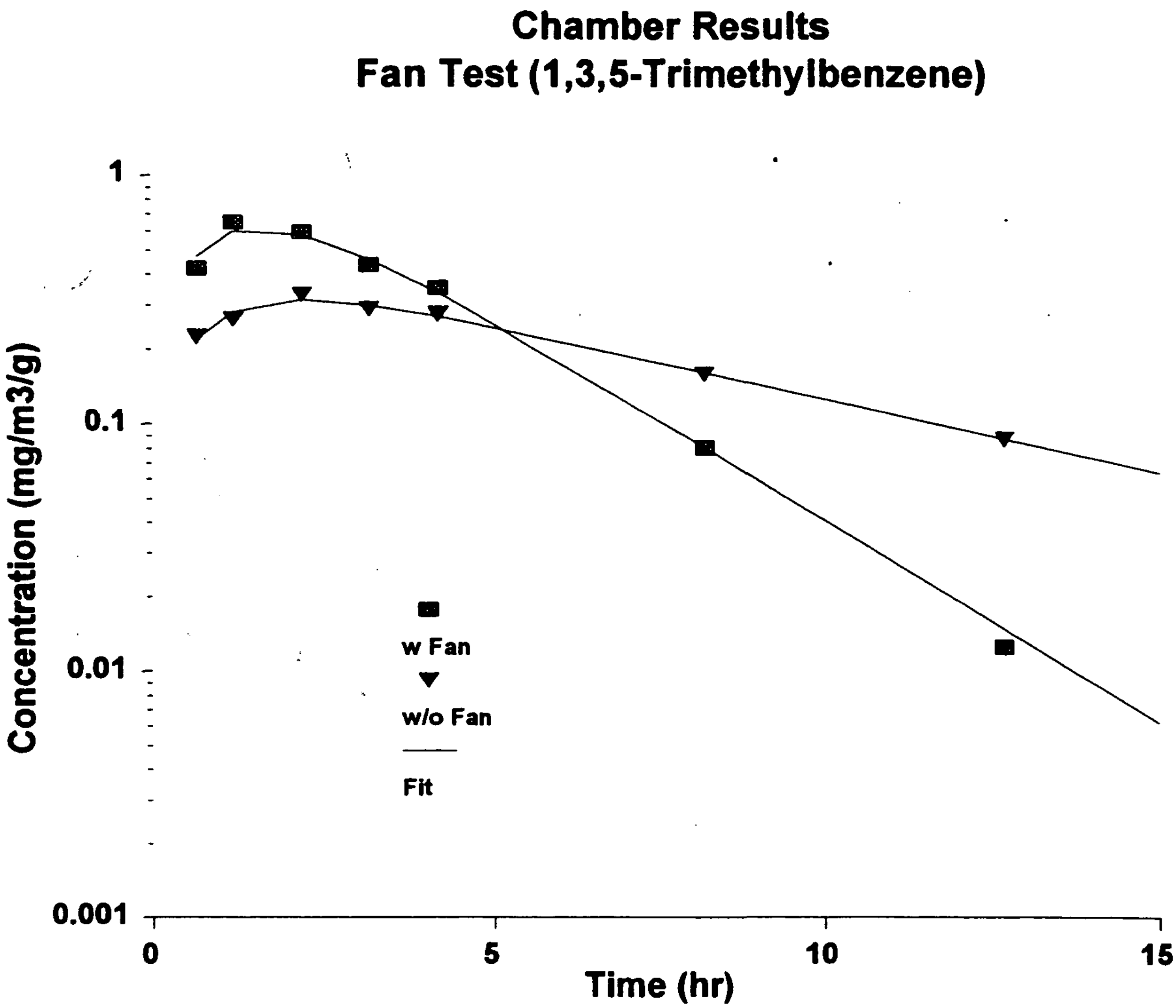

Chamber Results
Fan Test (o-Xylene)
Concentration (mg/m3/g)
10
1
0.1
0.01
0
5
10
15
Time (hr)
w Fan
w/o Fan
Fit

Chamber Results
Fan Test (Propylcyclohexane)

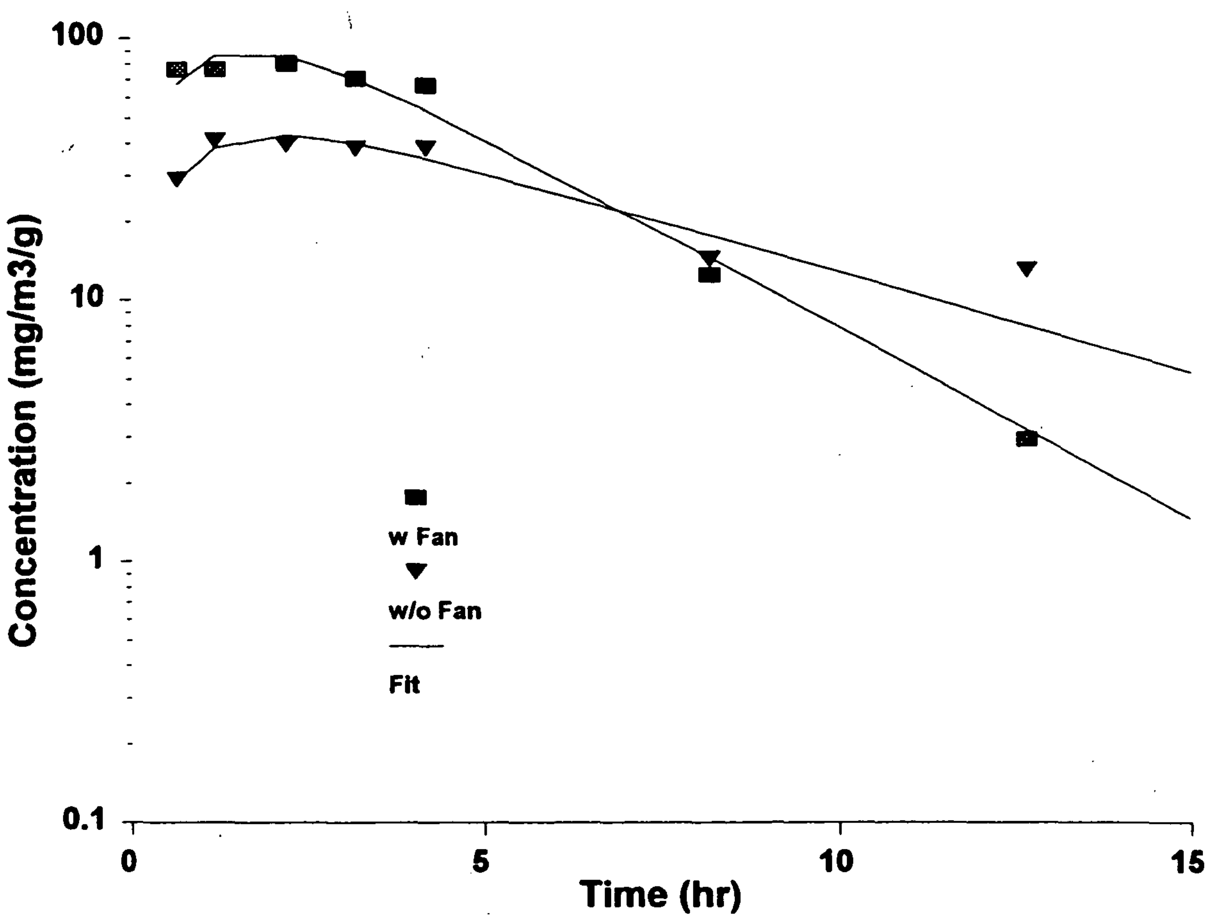


Chamber Results
Fan Test (3 & 4-Ethyltoluene)

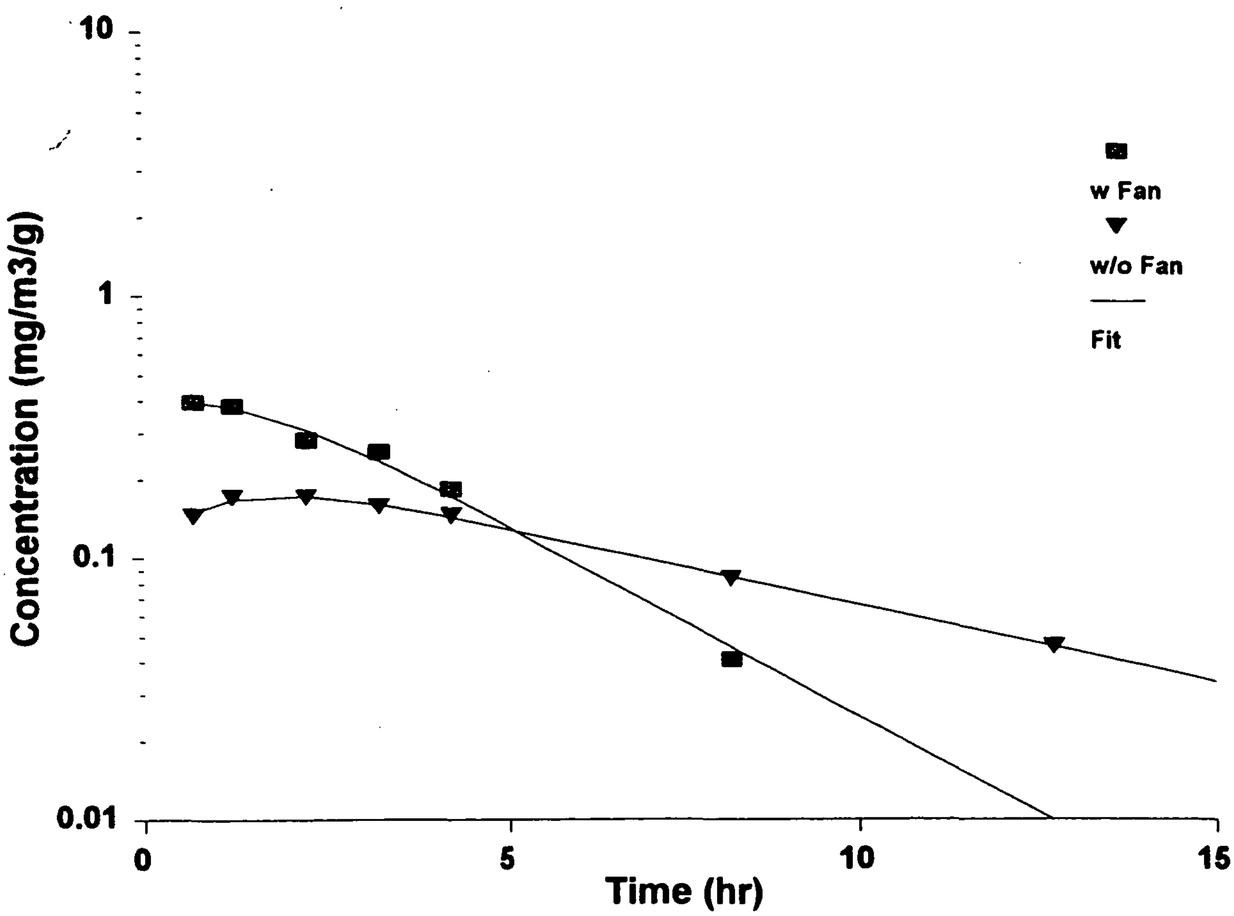



Chamber Results
Fan Test (1,3,5-Trimethylbenzene)
1
0.1
0.01
0.001
Concentration (mg/m3/g)
0
5
10
15
Time (hr)
w Fan
w/o Fan
Fit

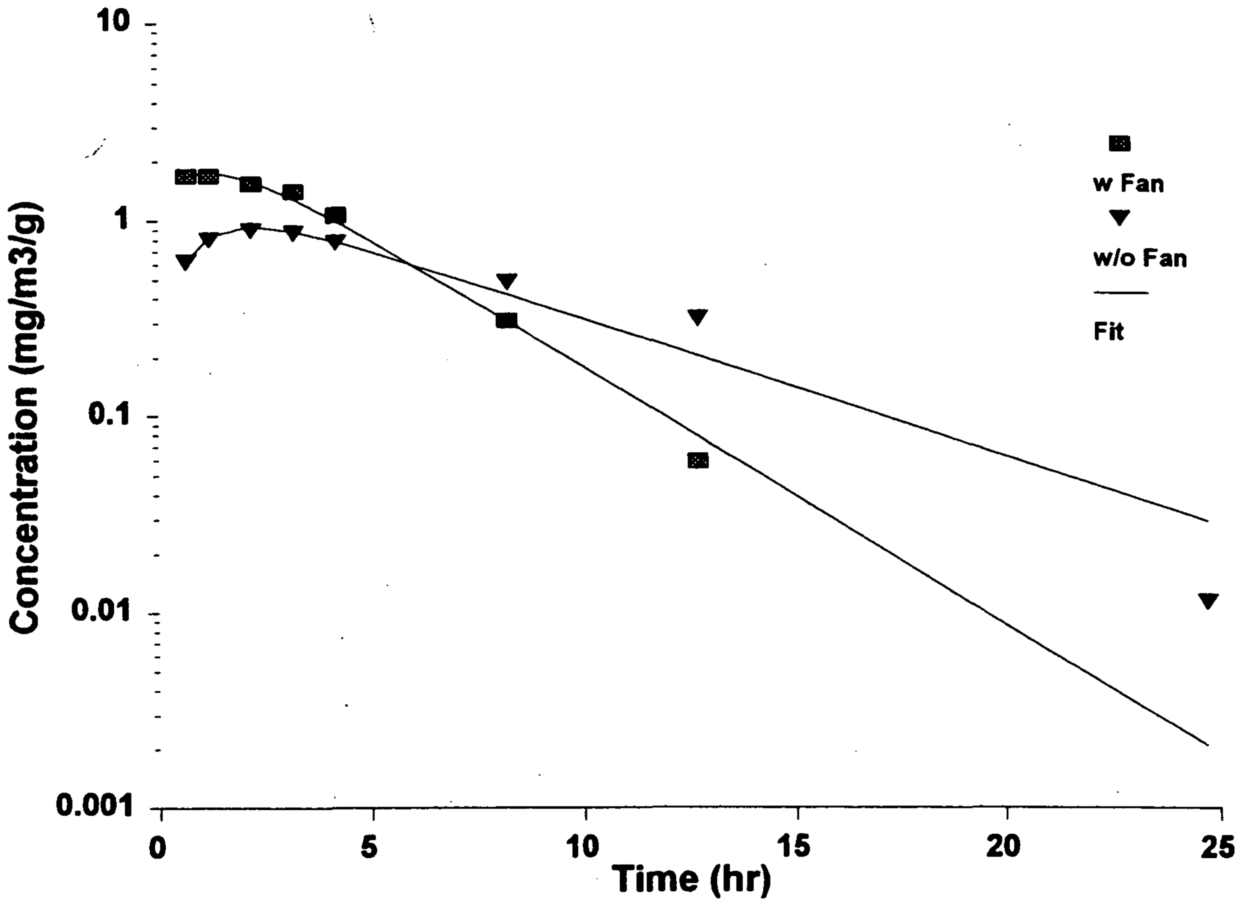
Chamber Results
Fan Test (n-Decane)

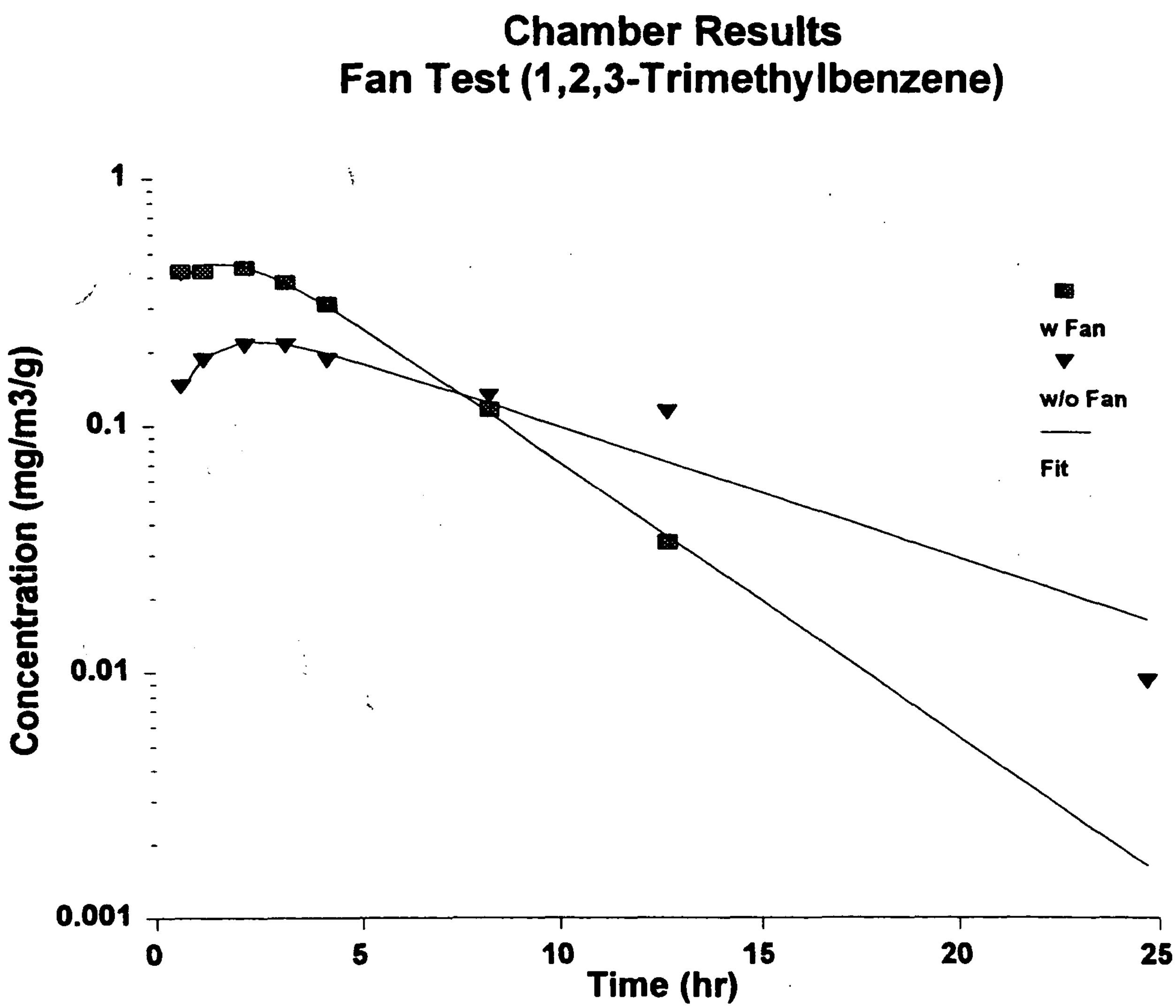


Chamber Results
Fan Test (2-Ethyltoluene)

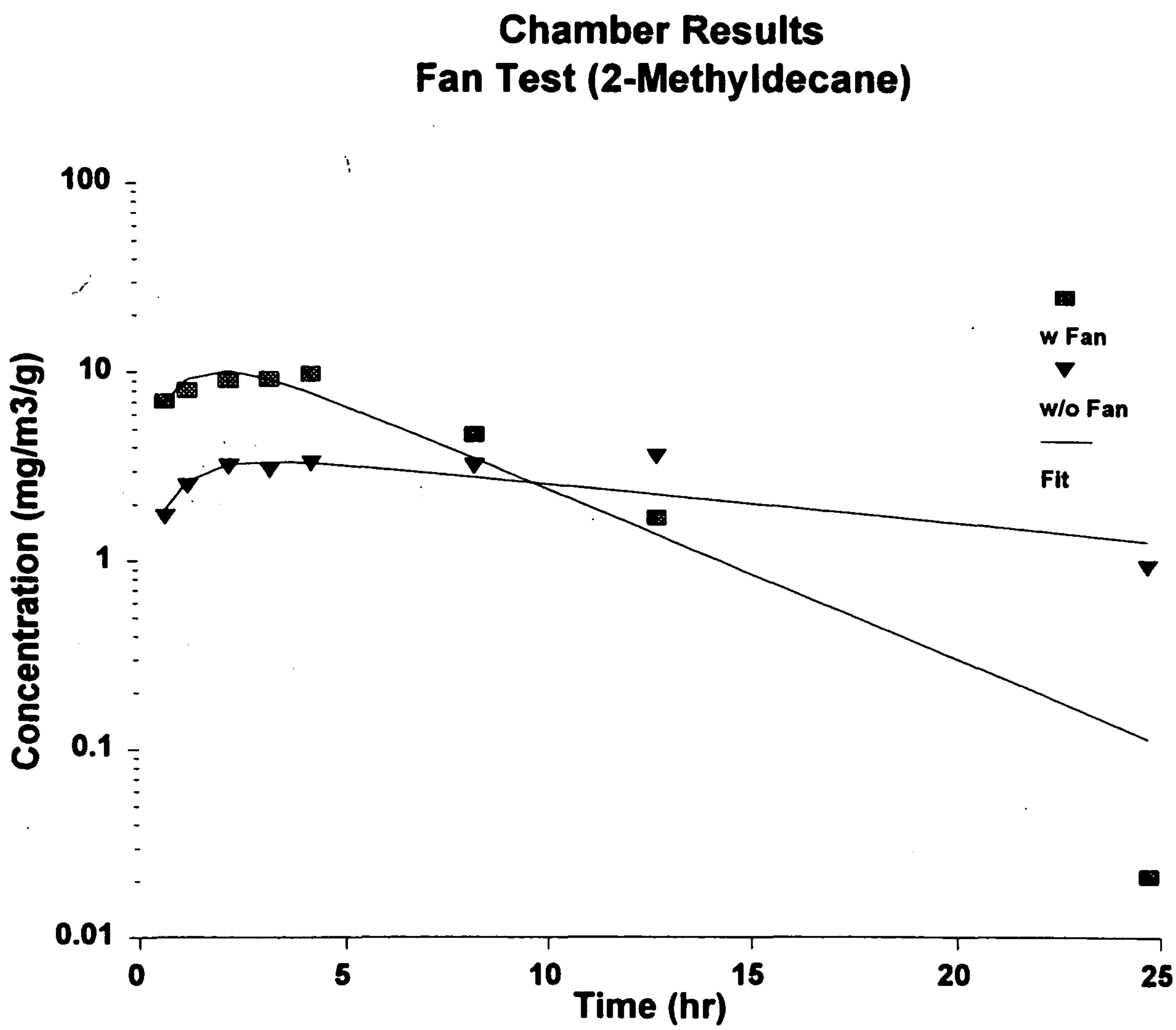


Chamber Results
Fan Test (1,2,4-Trimethylbenzene)



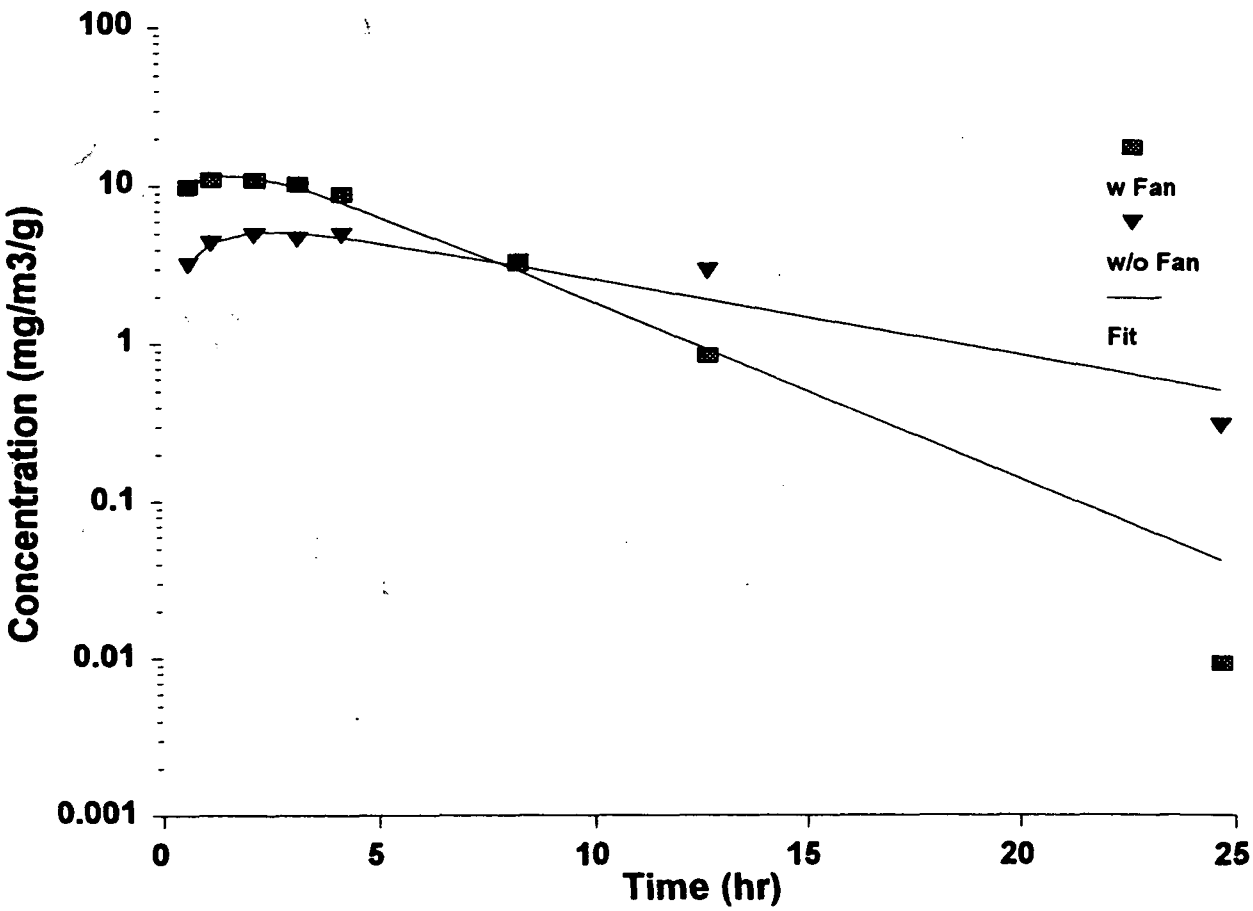


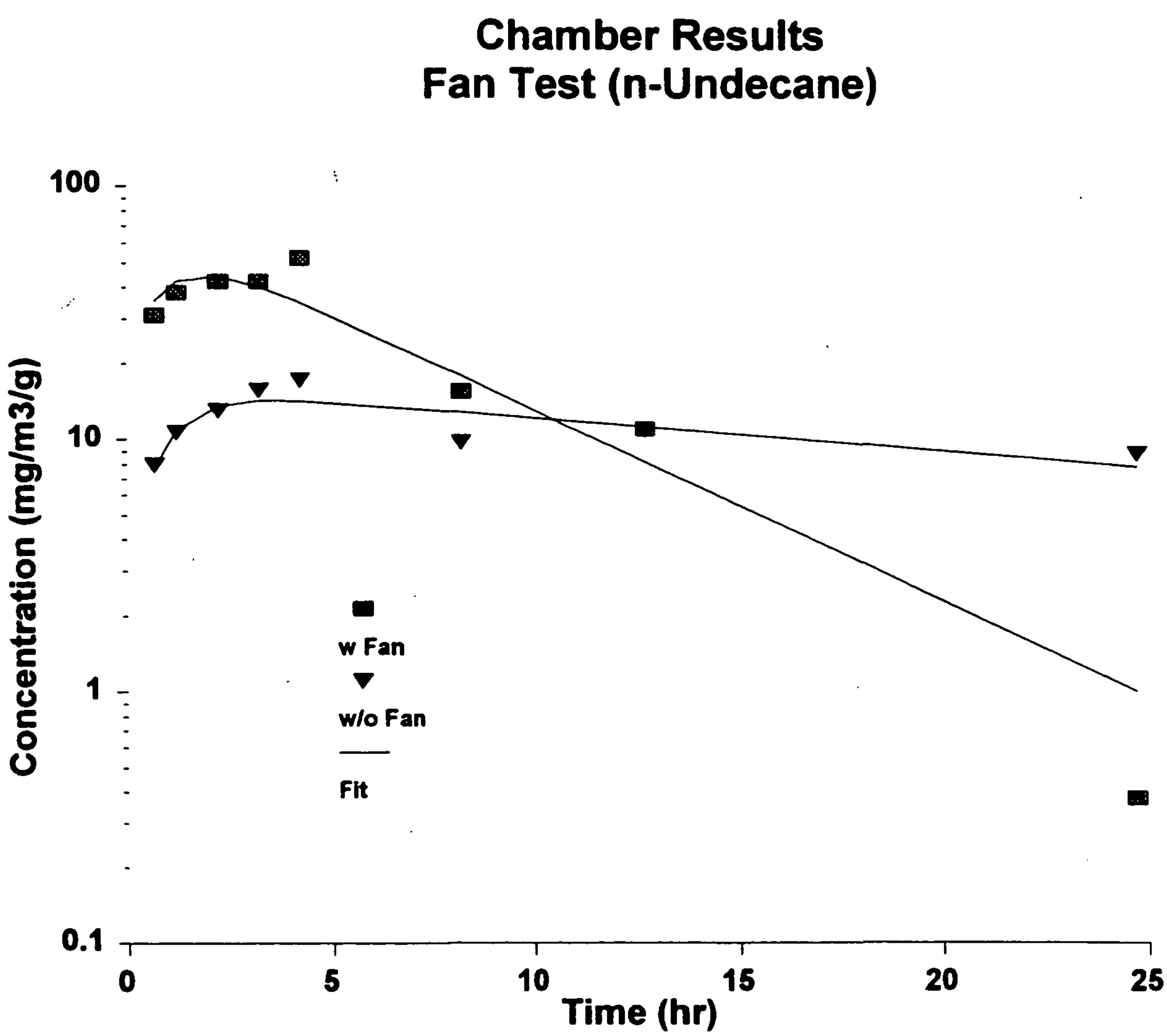
Chamber Results
Fan Test (1,2,3-Trimethylbenzene)
1
0.1
0.01
0.001
Concentration (mg/m3/g)
0
5
10
15
20
25
Time (hr)
w Fan
w/o Fan
Fit



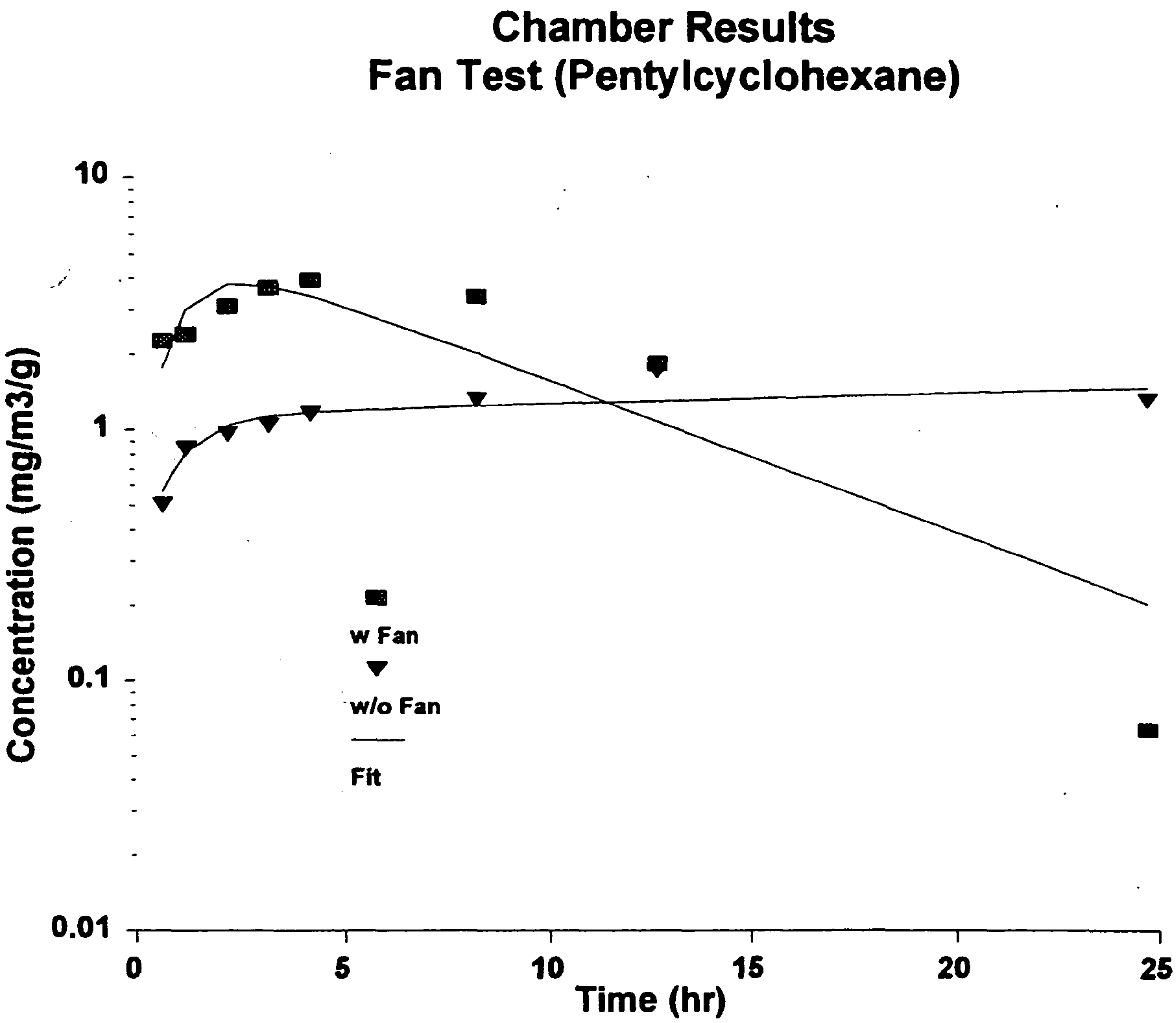
Chamber Results
Fan Test (2-Methyldecane)
100
10
1
0.1
0.01
Concentration (mg/m3/g)
0
5
10
15
20
25
Time (hr)
w Fan
w/o Fan
Fit

Chamber Results
Fan Test (trans-Decahydronaphthalene)

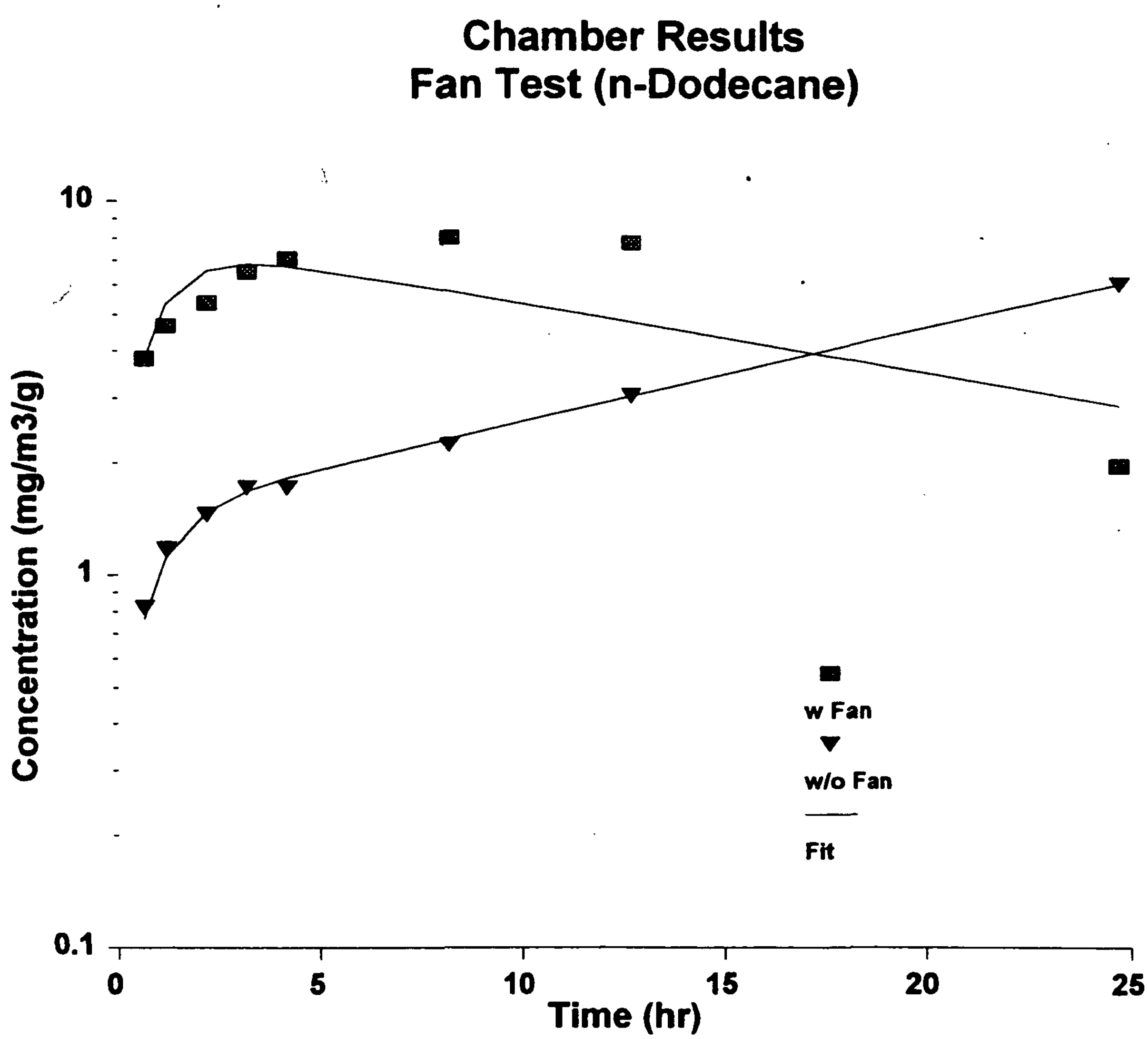




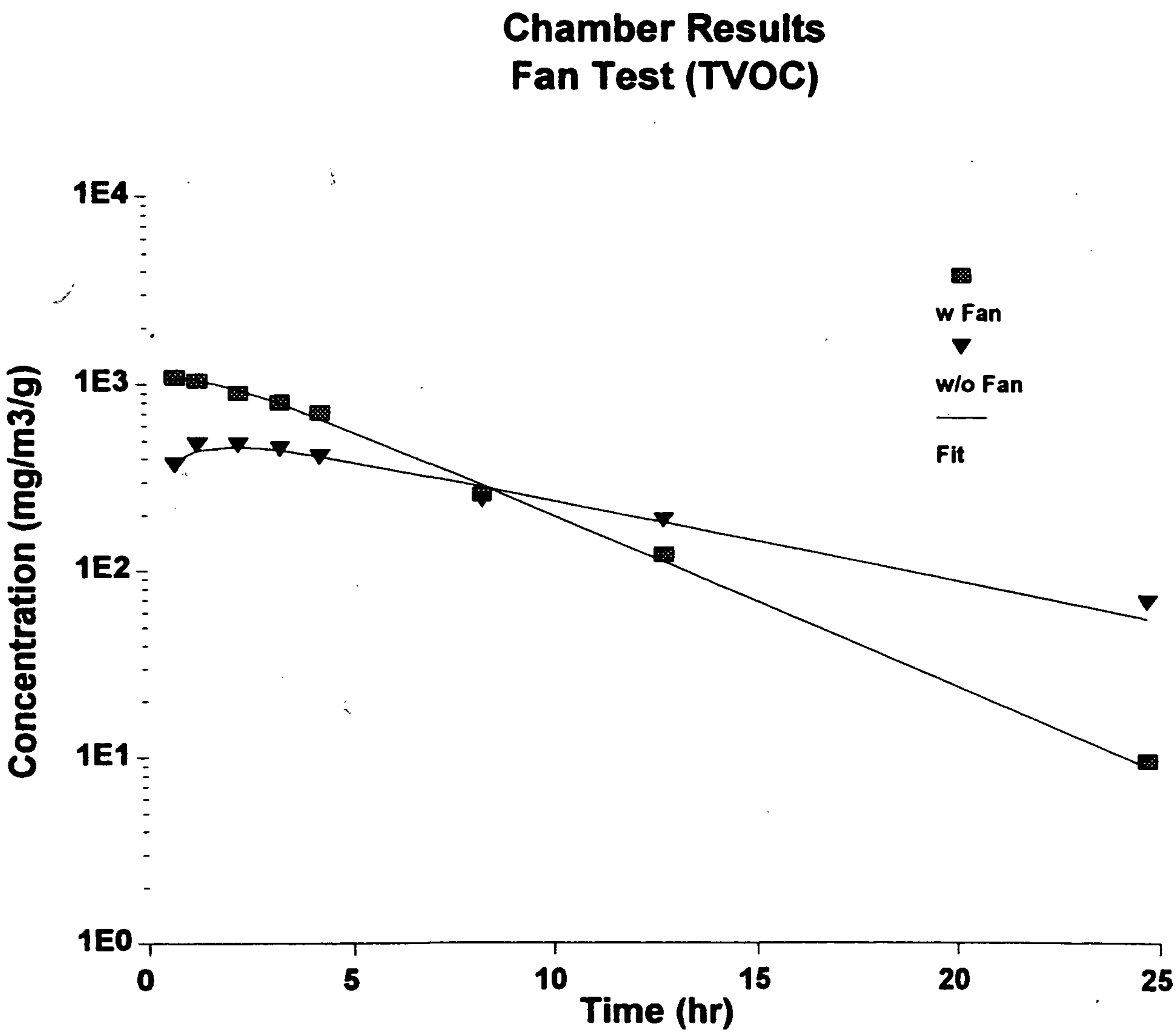
Chamber Results
Fan Test (n-Undecane)
100
10
1
0.1
Concentration (mg/m3/g)
0
5
10
15
20
25
Time (hr)
w Fan
w/o Fan
Fit



Chamber Results
Fan Test (Pentylcyclohexane)
10
1
0.1
0.01
Concentration (mg/m3/g)
0
5
10
15
20
25
Time (hr)
w Fan
w/o Fan
Fit



Chamber Results
Fan Test (n-Dodecane)
10
1
0.1
Concentration (mg/m3/g)
0
5
10
15
20
25
Time (hr)
w Fan
w/o Fan
Fit


Chamber Results
Fan Test (TVOC)
w Fan
w/o Fan
Fit
1E4
1E3
1E2
1E1
1E0
Concentration (mg/m3/g)
0
5
10
15
20
25
Time (hr)

LATEX PAINTS

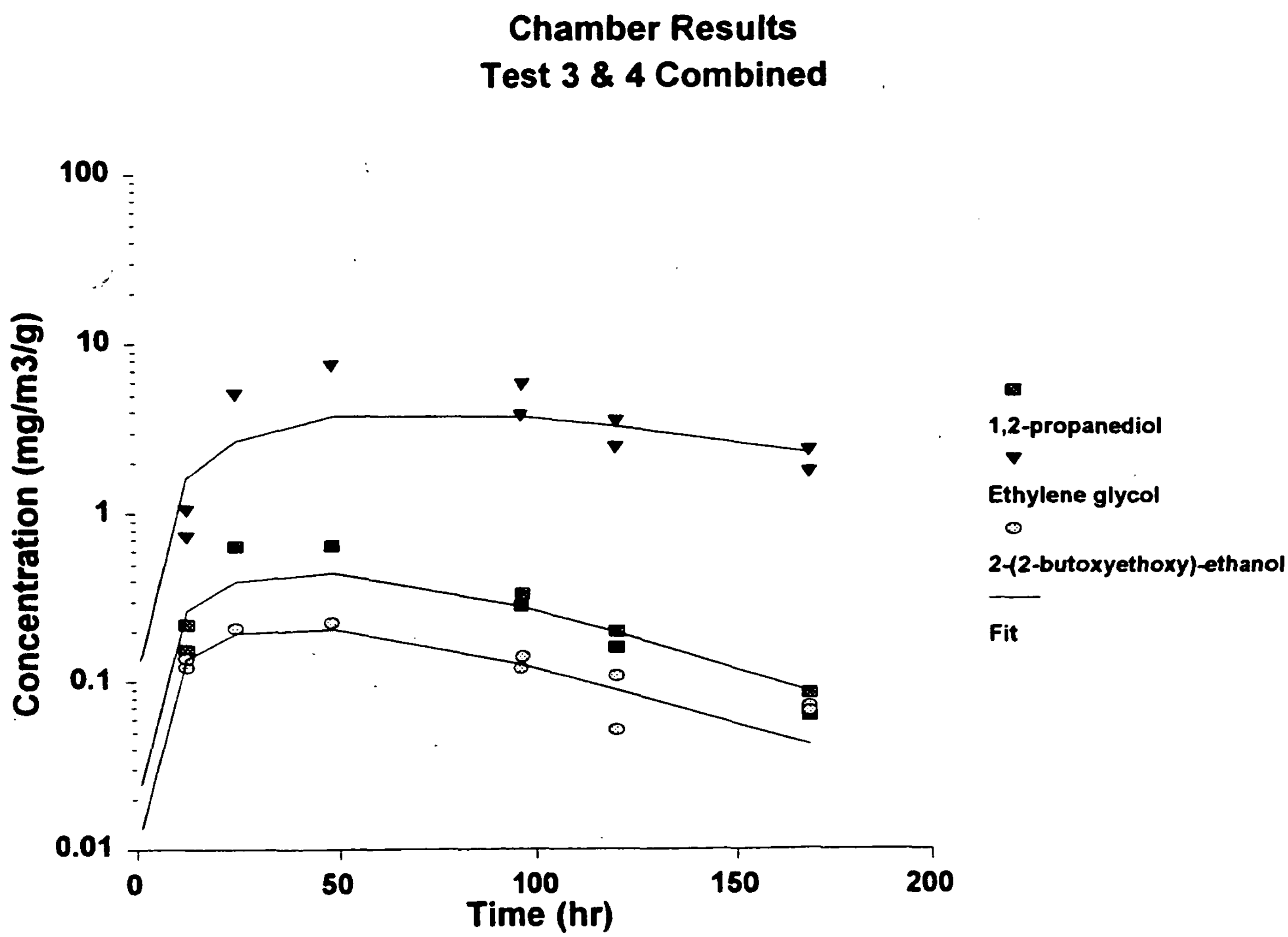
Chamber VOC Paint Study

TEST 3 & 4 Combined

Time hr	1,2-propane	Ethylene gly	2-(2-butoxye	Texanol	Formaldehyd	Acetaldehyd	TVOC
1.22				0.990	0.005	0.043	1.037
12.2	0.154	0.718	0.121	1.125	0.005	0.002	2.125
24.2	0.634	5.046	0.209	0.939	0.001	0.002	6.831
49.0					0.001	0.001	
96.5	0.329	5.73	0.140	0.634	0.000	0.001	6.834
120.2	0.159	2.40	0.0509	0.305	0.000	0.001	2.919
168.2	0.084	2.29	0.0700	0.456	0.000	0.001	2.900
1.25				1.37	0.005	0.028	1.408
12.2	0.220	1.032	0.138	1.175	0.006	0.002	2.572
24.23					0.001	0.001	
48.3	0.64	7.50	0.224	1.13	0.000	0.001	9.489
96.2	0.279	3.74	0.119	0.575	0.000	0.001	4.718
120.2	0.198	3.43	0.107	0.501	0.000	0.001	4.237
168.2	0.0609	1.71	0.0651	0.362	0.000	0.000	2.200
Sumsq	0.5210	2.3742	0.2494	0.5334	0.0209	0.0564	2.1567
Std	0.271	0.106	0.372	0.117	0.976	0.368	0.069
S0	5.05E-01	5.78E+00	3.95E-01	6.62E-02	5.13E-05	1.04E-04	2.21E+01
K	2.26E-02	1.41E-02	2.38E-02	8.02E-03	1.02E-02	1.14E-02	1.87E-02
K2	3.00E-03	1.40E-03	1.90E-03	9.07E-01	1.48E-02	1.12E-01	8.09E-04
Emission (mg/g)	2.62	36.99	1.23	14.22	0.08	0.53	48.83

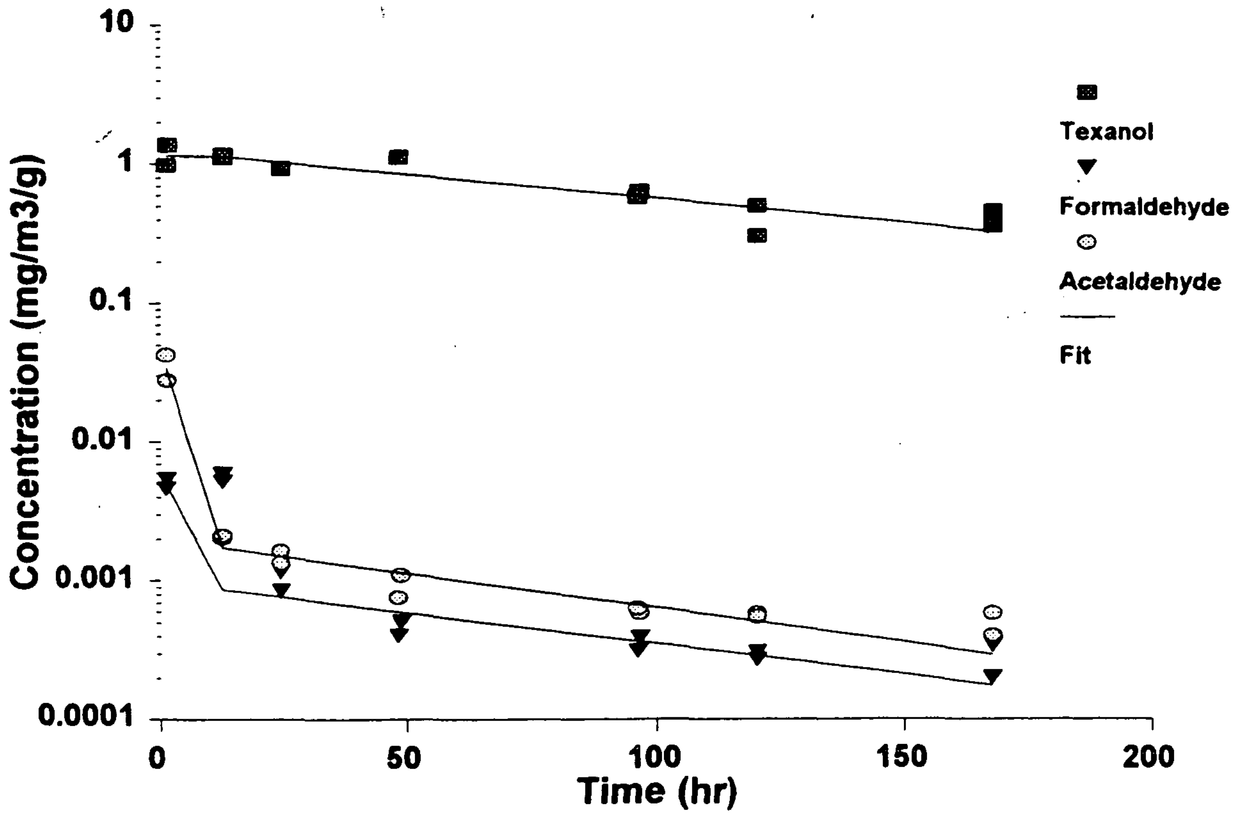
for texanol - acetaldehyde: **S(t) = S0 exp(-kt) with K2 = Concentration at t=0**

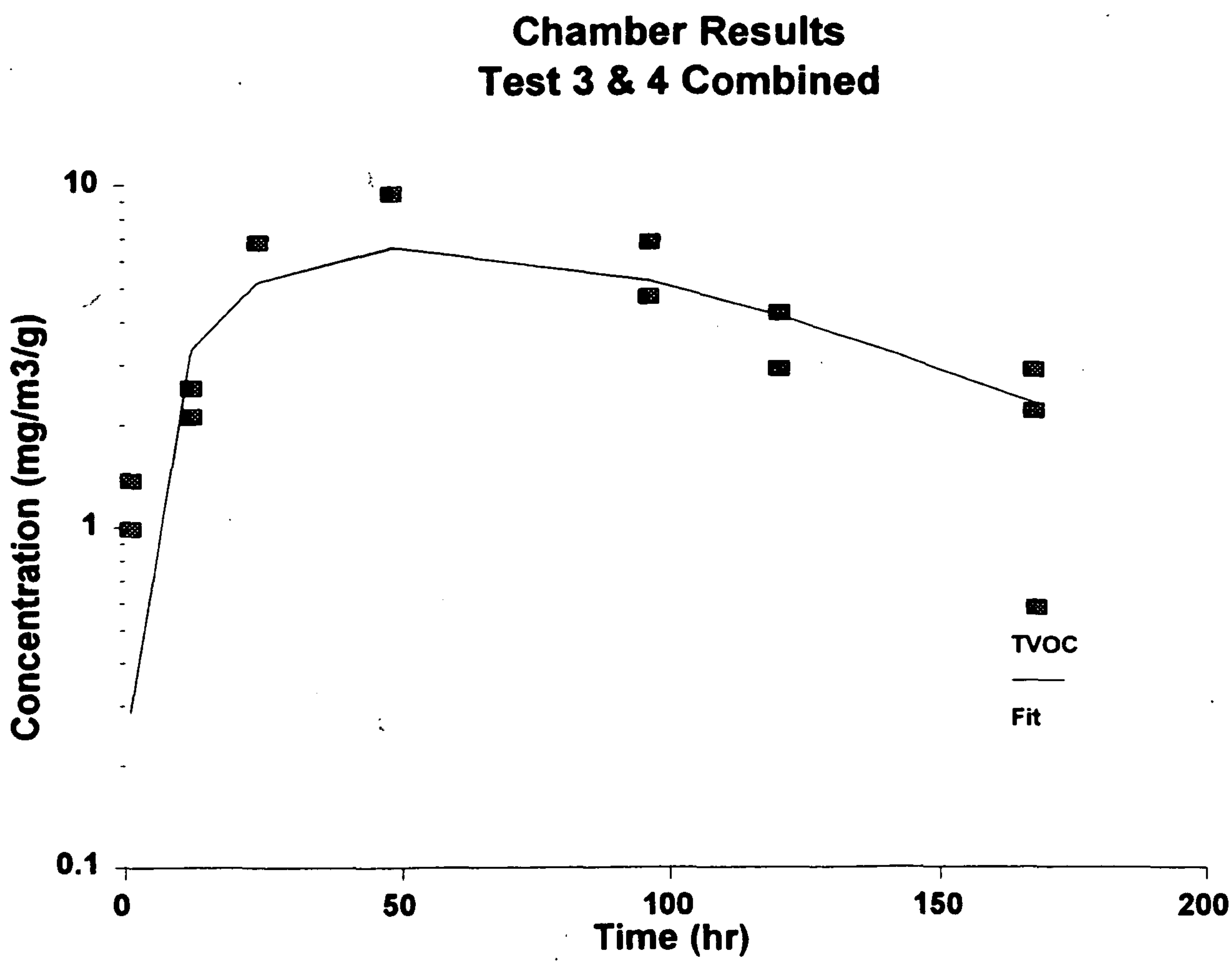
otherwise: **S(t) = S0 exp(-kt) [1 - exp(-k2t)]**



Chamber Results
Test 3 & 4 Combined
100
10
1
0.1
0.01
Concentration (mg/m3/g)
0
50
100
150
200
Time (hr)
1,2-propanediol
Ethylene glycol
2-(2-butoxyethoxy)-ethanol
Fit

Chamber Results
Test 3 & 4 Combined




Chamber Results
Test 3 & 4 Combined
Concentration (mg/m3/g)
10
1
0.1
0
50
100
150
200
Time (hr)
TVOC
Fit

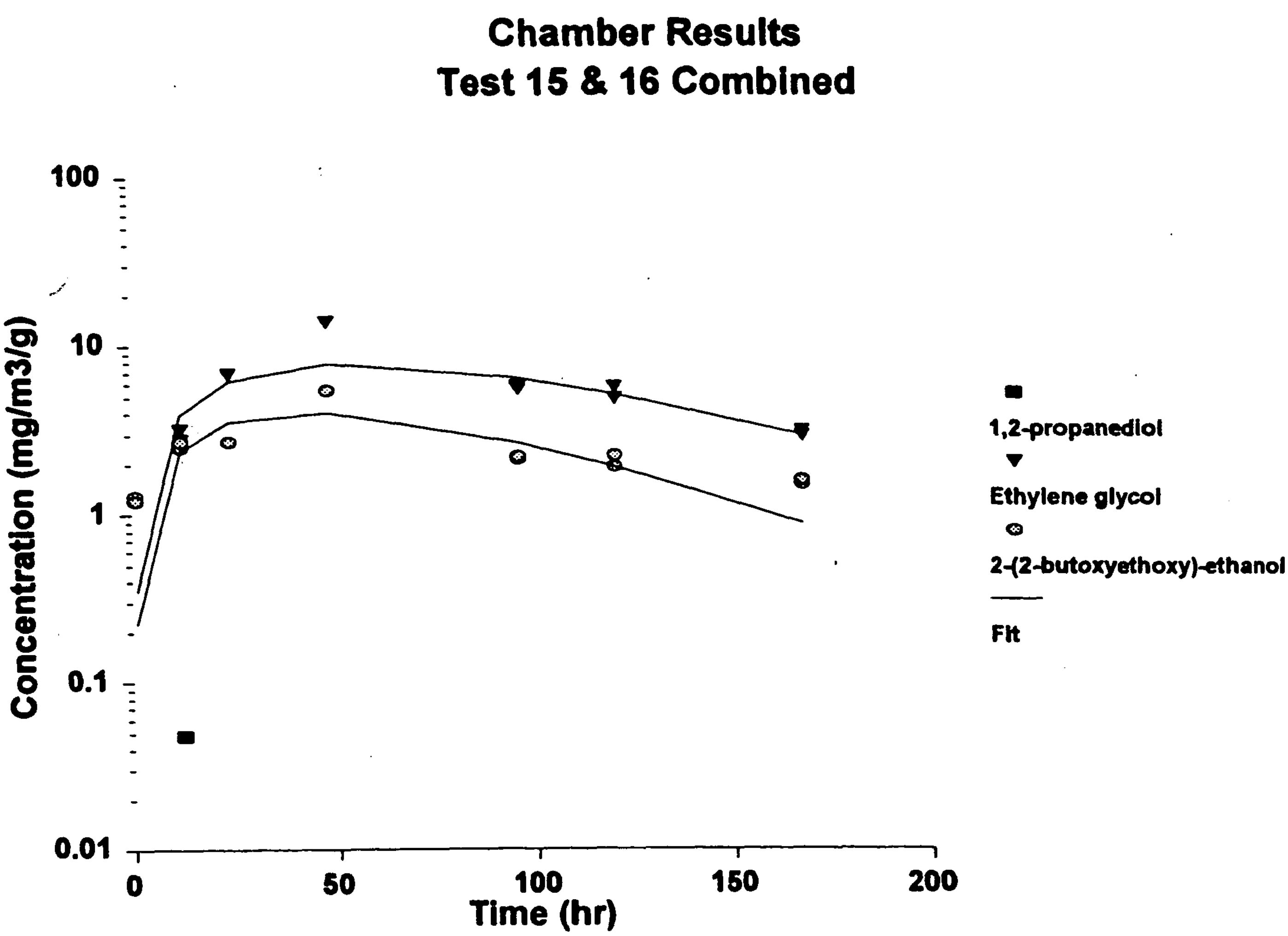
Chamber VOC Paint Study

TEST 15 & 16 Combined

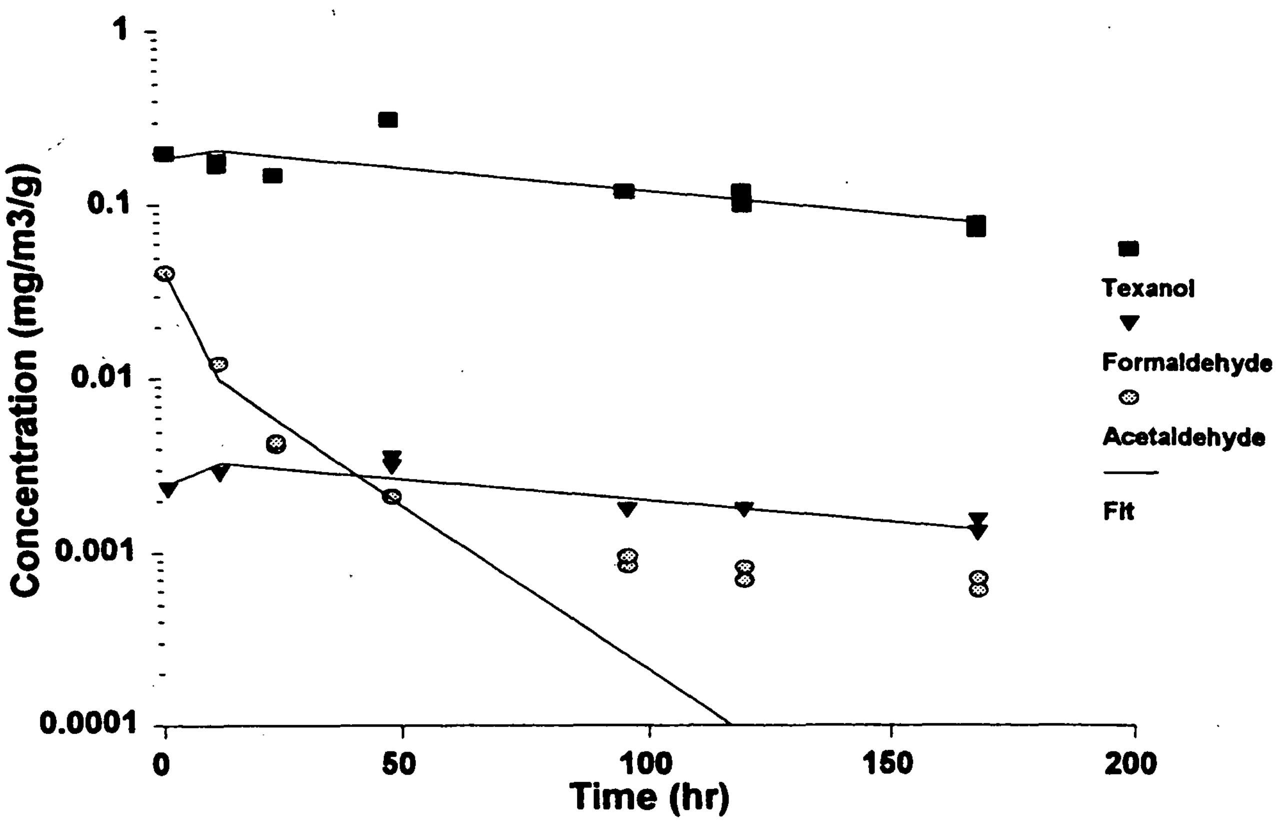
Time hr	1,2-propane	Ethylene gly	2-(2-butoxye	Texanol	Formaldehyd	Acetaldehyd	TVOC
1.3			1.283	0.200	0.002	0.041	1.526
12.3		2.801	2.511	0.170	0.003	0.012	5.497
24.3		6.875	2.697	0.150		0.004	9.726
48.3					0.004	0.002	
96.3		5.517	2.112	0.120	0.002	0.001	7.752
120.3		4.875	1.897	0.100	0.002	0.001	6.874
168.3		2.911	1.484	0.072	0.001	0.001	4.469
1.3			1.201	0.200		0.041	1.443
12.3	0.048	3.230	2.717	0.180		0.012	6.187
24.3						0.004	
48.3		13.991	5.477	0.310	0.003	0.002	19.783
96.3		5.757	2.166	0.120		0.001	8.044
120.3		5.618	2.228	0.120		0.001	7.966
168.3		3.101	1.575	0.078	0.002	0.001	4.756
Sumsq		1.8992	1.7089	0.3101	0.0198	0.0691	2.1820
Std		0.045	0.094	0.302	2.122	0.466	0.033
S0	5.05E-01	1.03E+01	4.10E+00	1.17E-02	1.84E-04	8.59E-04	3.12E+00
K	2.26E-02	1.77E-02	2.17E-02	6.17E-03	5.64E-03	4.39E-02	1.54E-02
K2	2.98E-03	2.02E-03	3.27E-03	1.00E-01	0.00E+00	1.04E-01	1.20E-02
Emission (mg/g)		59.79	24.66	2.76	0.03	0.14	88.24

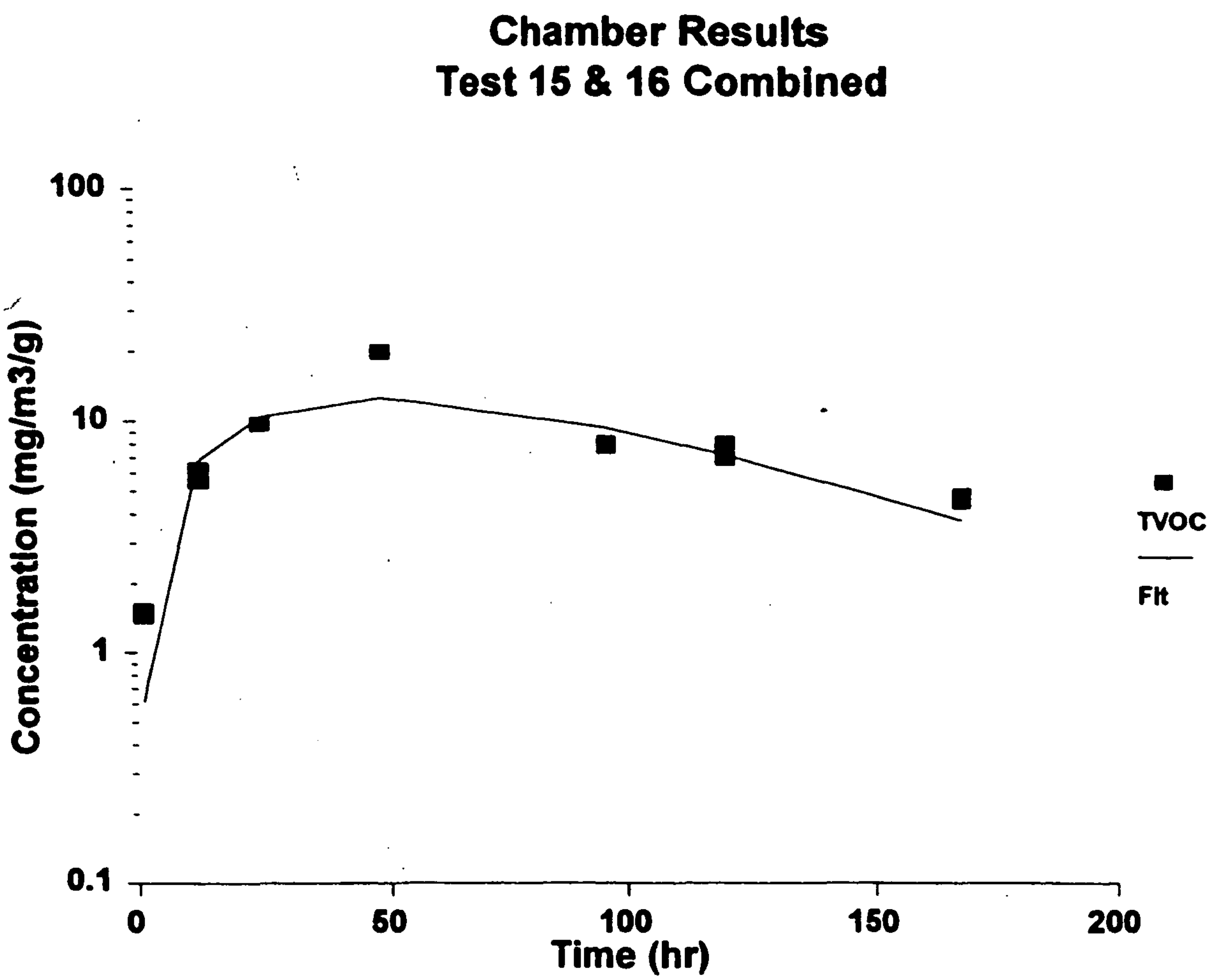
for texanol - acetaldehyde: $S(t) = S0 \exp(-kt)$ with K2 = Concentration at t=0

otherwise: $S(t) = S0 \exp(-kt) [1 - \exp(-k2t)]$


Chamber Results
Test 15 & 16 Combined
Concentration (mg/m3/g)
100
10
1
0.1
0.01
0
50
100
150
200
Time (hr)
1,2-propanediol
Ethylene glycol
2-(2-butoxyethoxy)-ethanol
Fit

Chamber Results
Test 15 & 16 Combined




Chamber Results
Test 15 & 16 Combined
100
10
1
0.1
Concentration (mg/m3/g)
0
50
100
150
200
Time (hr)
TVOC
Fit

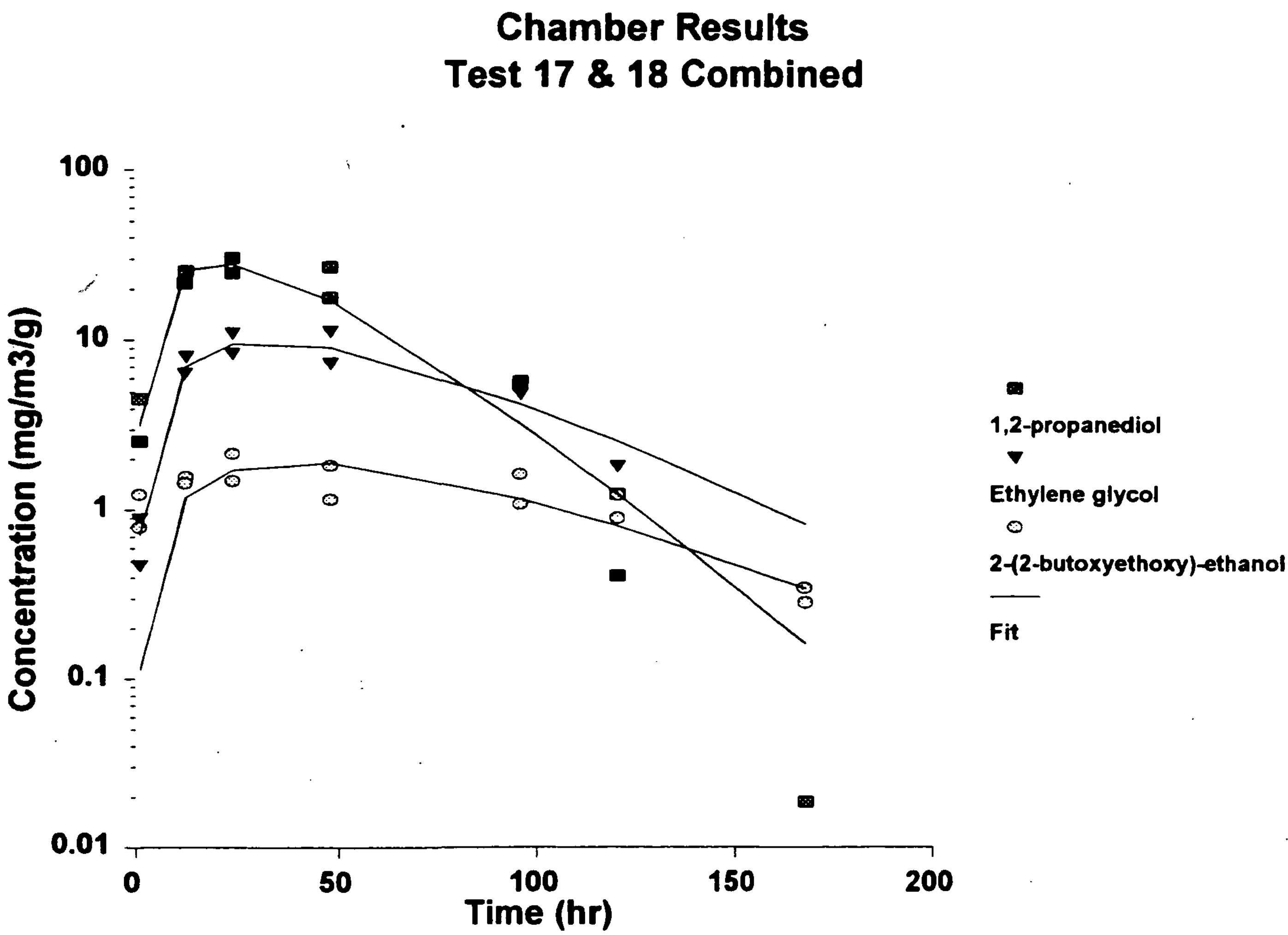
Chamber VOC Paint Study

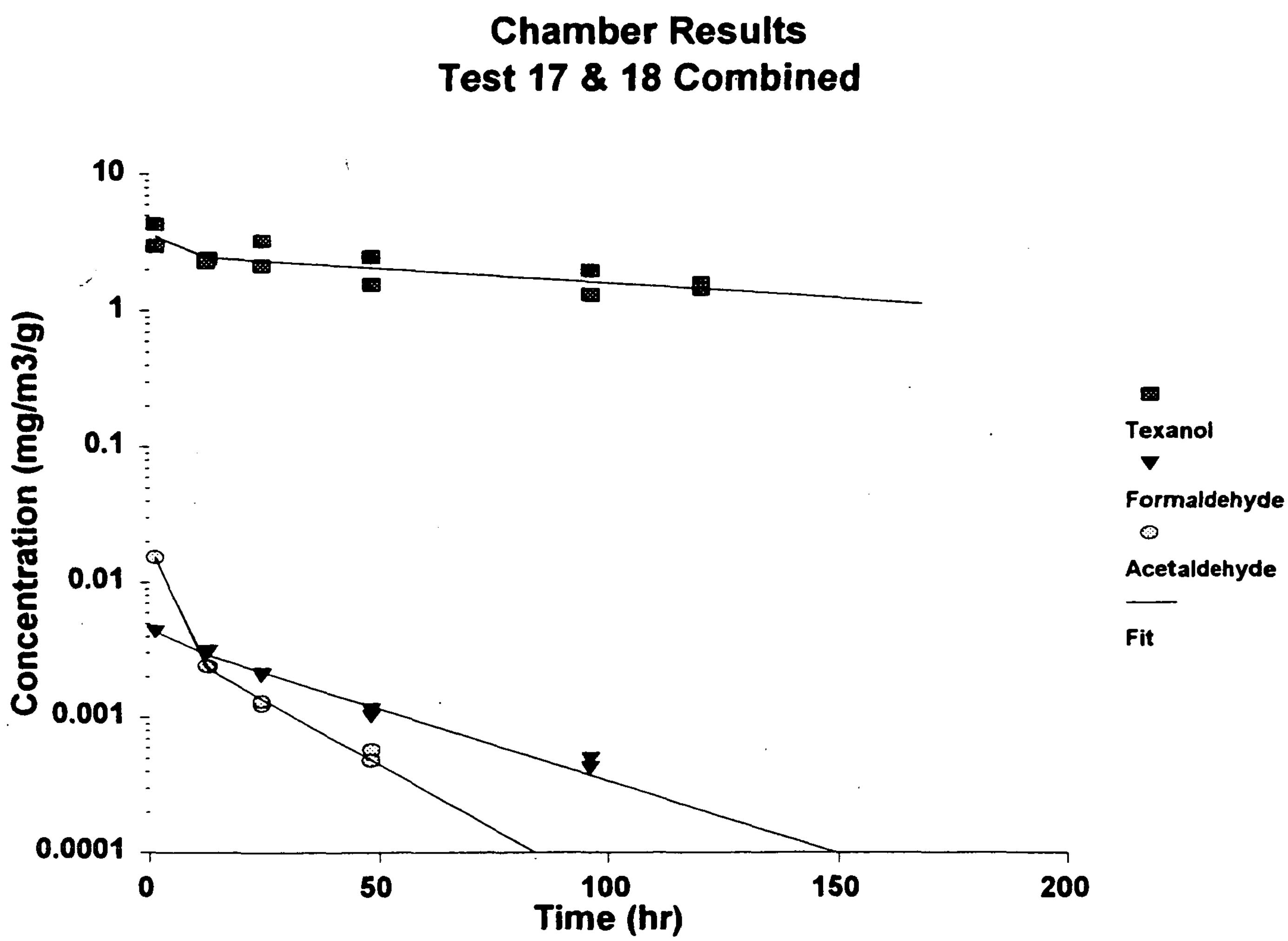
TEST 17 & 18 Combined

Time hr	1,2-propane	Ethylene gly	2-(2-butoxye	Texanol	Formaldehyd	Acetaldehyd	TVOC
1.3	4.51	0.88	1.23	4.33			10.946
12.7	25.6	8.01	1.57	2.42	3.090E-03	2.388E-03	37.627
24.3	30.6	11.1	2.16	3.25	2.107E-03	1.236E-03	47.115
48.3	27.1	11.3	1.84	2.46	1.138E-03	5.758E-04	
96.3	5.45	5.41	1.61	1.93	4.916E-04		14.408
120.3	0.405		0.889	1.42			2.714
168.3			0.340				0.340
1.3	2.53	0.469	0.787	2.99	4.343E-03	1.532E-02	6.793
12.3	21.7	6.42	1.44	2.27	3.016E-03	2.413E-03	31.811
24.3	25.0	8.38	1.48	2.13	2.051E-03	1.327E-03	
48.3	17.9	7.38	1.16	1.54	1.025E-03	4.825E-04	27.941
96.3	5.69	4.82	1.07	1.28	4.222E-04		12.864
120.3	1.23	1.79	1.21	1.59			5.814
168.3	0.02		0.280				0.298
Sumsq	3.2144	1.4651	1.6195	0.9745	0.0099	0.0064	3.5644
Std	0.030	0.041	0.208	0.068	0.803	0.169	0.023
S0	8.01E+01	4.57E+01	2.88E+00	1.37E-01	2.02E-04	2.02E-04	3.05E+02
K	4.81E-02	3.01E-02	2.36E-02	5.04E-03	2.46E-02	4.38E-02	4.15E-02
K2	2.39E-03	9.25E-04	2.33E-03	5.92E+00	5.79E-03	4.42E-02	8.37E-04
Emission (mg/g)	79.02	45.34	10.93	89.08	0.02	0.06	145.07

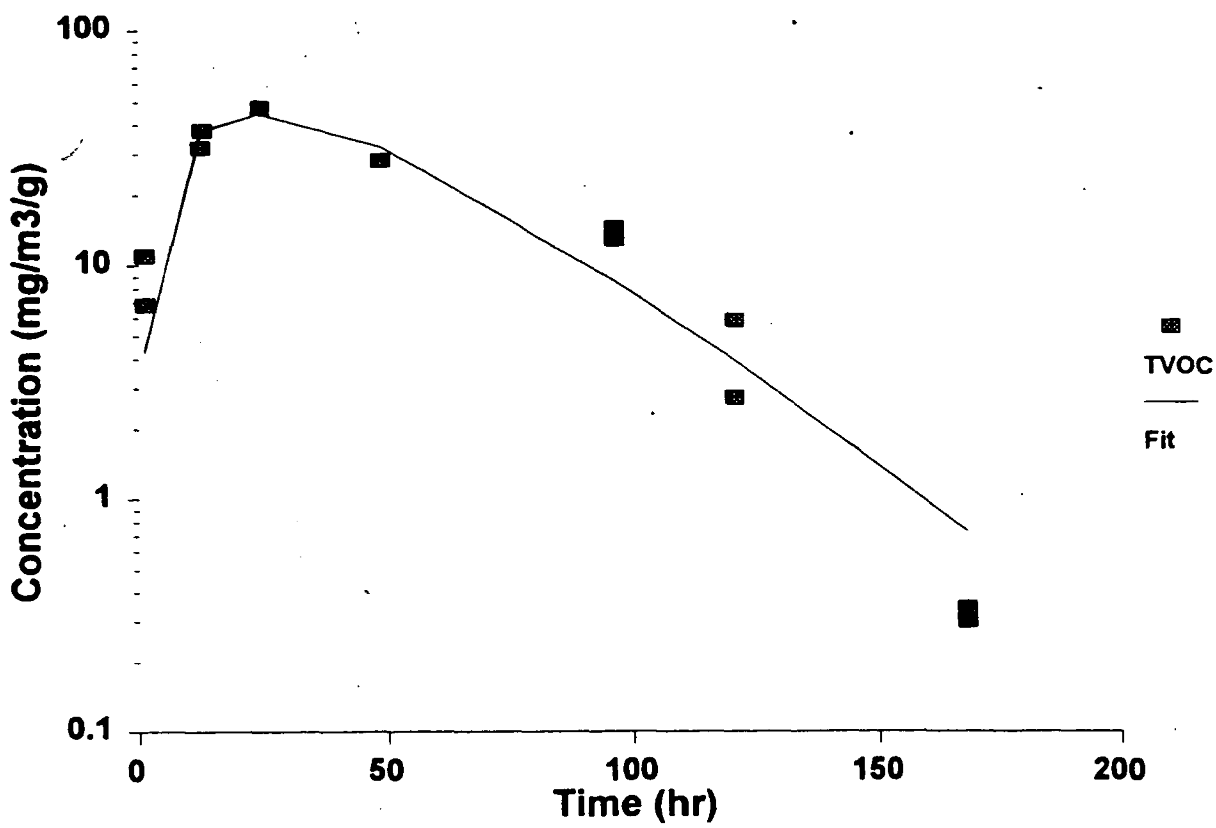
for texanol - acetaldehyde: **S(t) = S0 exp(-kt) with K2 = Concentration at t=0**

otherwise: **S(t) = S0 exp(-kt) [1 - exp(-k2t)]**


Chamber Results
Test 17 & 18 Combined
Concentration (mg/m3/g)
100
10
1
0.1
0.01
0
50
100
150
200
Time (hr)
1,2-propanediol
Ethylene glycol
2-(2-butoxyethoxy)-ethanol
Fit


Chamber Results
Test 17 & 18 Combined
Concentration (mg/m3/g)
10
1
0.1
0.01
0.001
0.0001
0
50
100
150
200
Time (hr)
Texanol
Formaldehyde
Acetaldehyde
Fit

Chamber Results
Test 17 & 18 Combined

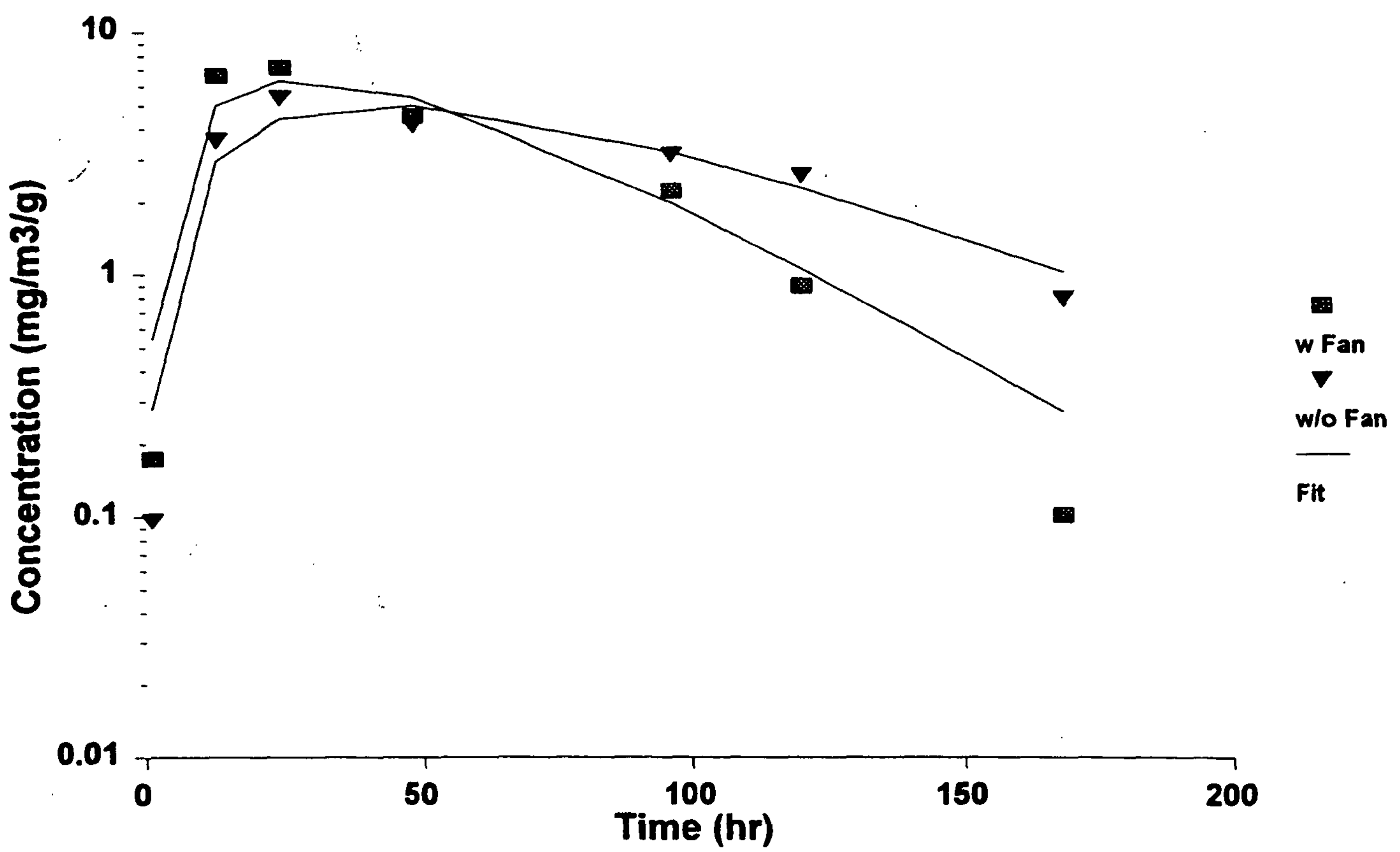


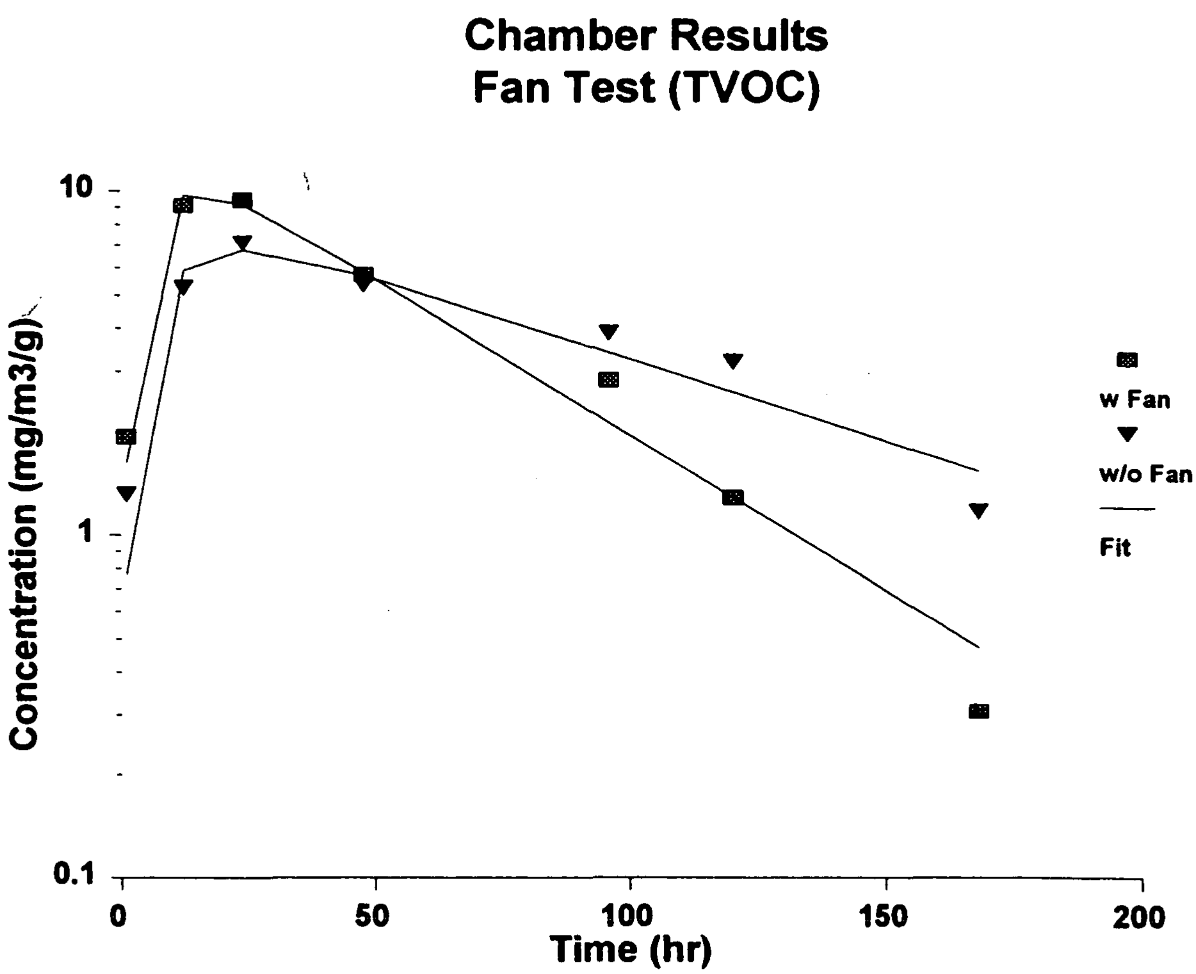
Chamber	VOC	Paint	Study				
	TEST 19 & 20 Combined		19 w fan	20 w/o fan			
Time	w Fan	w/o Fan					
hr	1,2-propane	Ethylene gly	2-(2-butoxye	Texanol	Formaldehyd	Acetaldehyd	TVOC
1.3	0.0421	0.174	0.097	1.604	2.738E-03	1.479E-02	1.934
12.7	0.840	6.632	0.291	1.298	1.533E-03	1.544E-03	9.064
24.3	0.773	7.200	0.270	1.142	6.243E-04	1.533E-03	9.388
48.3	0.342	4.499	0.152	0.698			5.691
96.3	0.062	2.221	0.082	0.437	7.448E-04		2.803
120.3	0.015	0.900	0.047	0.316	3.614E-04		1.278
168.3	0.005	0.102	0.018	0.182			0.306
1.3	0.030	0.10	0.043	1.1	2.689E-03	2.866E-02	1.314
12.3	0.48	3.6	0.21	0.96	2.358E-03	1.613E-03	5.239
24.3	0.59	5.4	0.20	0.86	3.491E-04	1.198E-03	7.058
48.3	0.38	4.1	0.15	0.65	2.736E-04		5.319
96.3	0.17	3.1	0.10	0.46	2.547E-04		3.861
120.3	0.094	2.6	0.080	0.43			3.189
168.3	0.015	0.80	0.046	0.31			1.170
Sumsq	0.3076	1.2110	0.0680	0.1304	0.0103	0.0000	0.5950
Std	0.150	0.069	0.095	0.033	1.890	0.001	0.026
S0	3.33E+00	4.01E+01	1.98E-02	7.86E-02	3.82E-05	8.20E-05	8.24E-01
K	5.38E-02	3.49E-02	1.74E-02	1.34E-02	3.85E-03	5.67E-04	2.10E-02
K2	1.67E-03	7.82E-04	3.50E-01	1.94E+00	7.97E-03	4.91E-02	1.24E-01
Emission (mg/g)	1.86	25.14	1.08	13.51	0.12	4.72	33.64
Sumsq	0.1819	0.8359	0.0309	0.0951	0.0019	0.0000	0.7908
Std	0.126	0.069	0.061	0.035	0.360	0.000	0.046
S0	1.94E+00	2.40E+01	1.31E-02	5.36E-02	1.91E-05	1.12E-04	5.08E-01
K	3.63E-02	2.32E-02	9.85E-03	7.91E-03	4.11E-03	2.48E-02	1.10E-02
K2	1.46E-03	6.90E-04	2.25E-01	1.37E+00	8.48E-03	9.48E-02	9.54E-02
Emission (mg/g)	2.06	29.96	1.27	15.90	0.11	0.21	41.47

for texanol - acetaldehyde: **$S(t) = S0 \exp(-kt)$ with K2 = Concentration at $t=0$**

otherwise: **$S(t) = S0 \exp(-kt) [1 - \exp(-k2t)]$**

Chamber Results
Fan Test (Ethylene Glycol)




Chamber Results
Fan Test (TVOC)
10
1
0.1
Concentration (mg/m3/g)
0
50
100
150
200
Time (hr)
w Fan
w/o Fan
Fit

APPENDIX E

METALS DATA PROVIDED BY EPA/NERL

date: 9/28/93 XRF-222

re: XRF Screening Report of HQ Paint Samples

from: Dr. T. M. Spittler

to: Donald H. Whitaker

Twenty samples were submitted for screening for heavy metals using the Kevex XRF analyser. Samples were homogenized and an aliquot was analysed using target #4 and target #2 conditions. Quantitation was performed using a low level AA reference solution (6-120 ppm). This standard contained PB,Cd,Se,As, Cr,Ag,Tl,Mn,Zn,Cu, Ni, Co, V and Sb). Quantitation of Ca, Fe, I, Zr and Br was done using standards prepared in our lab. Only elements found above instrument background are reported here.

Sample #	Field ID	Cr*	Mn	Ni	Cu	Zn	Pb	Bi	Co
21221	First Star	<5	15	10	9	6	<10		
21222	Bumbershoot				24				
21223	Sherrif's Star		15		6	5	30	10	
21224	Violet Veil			5	10	5	33		
21225	Hyacinth				66	5	21		125
21226	Crescent Green	10		7	6	9	10		
21227	Coral Canyon			5	9	6	30		
21228	Grass Roots				435				
21229	Praline	9		4	10	9	12		
21230	Marmalade	9		7	5	34	<5***		
21231	Tomahawk	13		4	7	4	<5		
21232	Dawn Yonder	7		8	172	8	9		
21233	Vibrant Violet		7	7	49	69	12		
21234	Orange Ice			5	7	5	12		
21235	Ice Cap			5	34	4	<10		
21236	Orange Glaze			5	8	7	<10		
21237	Rose Dawn			10	7	48	<5		
21238	Chim Cham	15	12	7	8	7	10		
21239	Seafoam				[5]	2680	<10		
21240	Antigua		15	7	15	8	12		

Lab ID	Ca%	Ti%	Fe	Br	I	Zr	Hg**
21221	10.5	14.6	540				
21222		40.0	500	700			
21223		50.0	3050			250	
21224	4.6	28.5	470				
21225		45.0	150			310	
21226	10.5	14.0	2500				
21227	5.0	29.8	3800				
21228		6.8	2280	1.7%			
21229	2.0	10.0	6080				<10
21230		6.7	760				<10
21231	5.4	1.2	6800				<10
21232		1.5	640	34			10
21233	1.9	9.6	504				
21234		15.8	308		1400		<10
21235		16.1	1060	16			
21236		34.0	6840		1600		
21237		27.0	240				<10
21238	10.0	11.2	1500			140	
21239	8.7	26.0	950			340	
21240	15.5	15.0	630			100	

* All values in ppm by weight unless noted otherwise.

** Hg values are possibly low because of evaporation of organic mercury compounds while samples are in the analytical chamber. However, Sample 21226 (reported to have high Hg) was rerun with no time delay for evaporative loss and still showed no measureable level of Hg above 5 ppm.

No detectable levels of V, As, Se, Sn, (see note below) Mo, Cd, Sb or Ba. Al not quantifiable on Kevex instrument. No attempt made to measure Cl or S.

Sample 21226 was reported to have high Sn. This sample was rerun for five times as long to recheck Sn level. No Sn was detected at the 5 ppm level.

*** In some samples detection limit is lower than others because of absence of interfering elements.

Listing of samples for XRF analysis:

GL6987-20573-LAGO-05	(ORANGE ICE)
GL6918-16112-LAGO-23	(ORANGE GLAZE)
GL3480-01044-LCFR-27	(TOMAHAWK)
GL6300-64542-LASB-04	(ICE CAP)
GL6380-64984-LASB-24	(DOWN YONDER)
GL8000-46212-ADSG-25	(SEAFOAM)
GL4550-76262-ADGP-27	(HYACINTH)
GL5700-25312-ADFY-26	(CHIM CHAM)
GL4550-20852-ADGX-06	(SHERIFF'S STAR)
GL5718-34722-ADFG-09	(ANTIGUA)
SW200-1734-LVFG-08	(GRASS ROOTS)
SW200-1604-LCGR-28	(ROSE DAWN)
SW200-1545-LCSP-23	(VIBRANT VIOLET)
SW200-1629-LVFO-24	(MARMALADE)
SW200-1125-LCSX-03	(PRALINE)
SW200-1435-ADGG-28	(BUMBERSHOOT)
SW200-1529-ADSB-28	(VIOLET VEIL)
SW200-1003-ADFX-03	(FIRST STAR)
SW200-1352-ADFY-21	(CRESCENT CREAM)
SW200-1309-ADSX-03	(CORAL CANYON)